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CYCLOADDITIONS OF METHYLENECYCLOPROPANES AND STRAINED BICYCLO[n.1.0]ALKANES TO RADICOPHILIC OLEFINS

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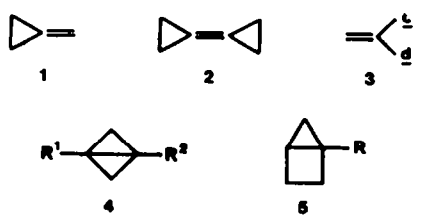
Abstract. The methylenecyclopropanes **1**, **2**, **11** upon reaction with α-donorsubstituted acrylonitriles **3a**, **3c** gave two types of products, regular [2+2] cycloadducts **6**, **8**, **10**, **13**, **14** and thiacyclopentane derivatives **7**, **9**. The capto-dative substituted methylenecyclopropane **12** preferentially homodimerized to **15** even in the presence of **2**. The capto-dative olefin **3a** also added across the central single bonds of a bicyclo[1.1.0.]butane derivative **4b** and bicyclo[2.1.0]pentane **5a** to yield **16** and **19** via diradical intermediates.

INTRODUCTION

The strained methylenecyclopropane (**1**)[1] and bicyclopropylidene (**2**)[2] as well as capto-dative olefins[3,4] are either sterically or electronically activated to undergo [2+2] cycloaddition reactions via diradical intermediates. Both types of olefins **1**, **2**, as well as **3**[5] may thermally head-to-head cyclodimerize or add to other suitable olefins, allenes or dienes.

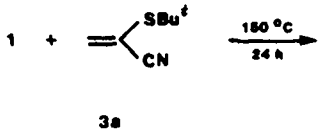


We here report the first reactions of capto-dative olefins **3** with **1** and **2** as well as with a bicyclo[1.1.0] butane derivative **4** and bicyclo[2.1.0]pentane (**5**), two bicyclic systems which are known to react across their most highly strained, central single bond via diradical intermediates.[6-8]

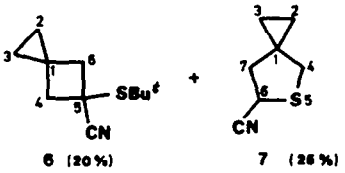
Cycloadditions of 1 and 2 to capto-dative olefins 3

While α-tert-butylthioacrylonitrile (**3a**) readily dimerizes, slowly even at 0°C, in a reversible [2+2] head-to-head cycloaddition, it gives two products when heated with methylenecyclopropane (**1**) to 150°C. One is the regular [2+2] cycloadduct, 5-tert-butylthiospiro[2.3]hexan-5-carbonitrile (**6**) (20%), the other, 5-thiaspiro-[2.4]heptan-6-carbonitrile (**7**) (25%),

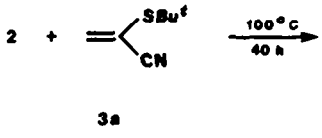
apparently arises from isobutene elimination in the intermediate. Bicyclopropylidene (**2**), upon reaction with **3a** follows an analogous route, albeit at lower temperature (100°C) to yield 8-tert-butylthiodispiro[2.0.2.2]octan-8-carbonitrile (**8**) (34% isolated) and 7-thiadispiro[2.0.2.3]nonan-8-carbonitrile (**9**) (24%). The ratio of **8** to **9**, as determined by gas chromatography in the crude mixture, was 3:1. Both the more rapidly dimerizing α-phenylthioacrylonitrile (**3b**) and the less reactive α-methoxyacrylonitrile (**3c**) gave only intractable mixtures with methylenecyclopropane (**1**).



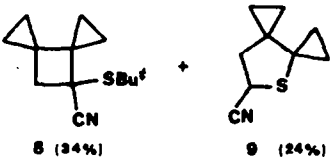
3a



6 (20%) **7** (25%)



3a

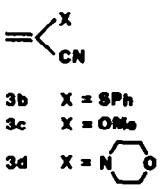


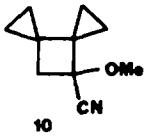
8 (34%) **9** (24%)

Bicyclopropylidene (**2**), however, cleanly underwent a formal [2+2] cycloaddition with **3c** to yield 2-methoxydispiro[2.0.2.2]octancarbonitrile (**10**) (59%), isolated as a colourless oil by preparative gas chromatography and identified - like the other cycloadducts - by its ^{1}H NMR spectrum. The α-morpholinoacrylonitrile (**3d**) gave only intractable mixtures with both olefins **1** and **2**.

The acceptor-substituted methylenecyclopropane derivative **11**,[9] noted for its extreme reactivity in Diels-Alder- and Michael-additions,[10,11] readily cycloadded to **3a** yielding a 1:2.2 mixture of two isomeric products (63% isolated). According to its high field ^{1}H NMR spectrum, this mixture most probably consisted of the two regioisomeric [2+2] cycloadducts **13** and **14** rather than the two conceivable diastereomers of the head-to-head cycloadduct **13**. This assignment rests on the fact that one of the cyclobutane methylene signals (6- and 5-H, respectively), which show up as two AB line patterns, has a larger chemical shift difference ($|\Delta\delta = 0.78$) and is centered at lower field (2.38) while the other is centered at higher field (2.32) with a $|\Delta\delta$ of only 0.29 ppm. Therefore the latter signal, corresponding to the major isomer, was assigned to 5-H_2 in **13**.

Surprisingly, the methylenecyclopropane derivative **12**[11] with its





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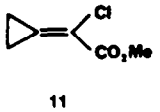
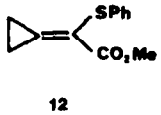


11



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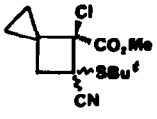

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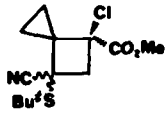

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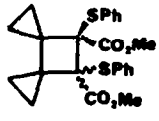


15

capto-dative substitution pattern did not add to bicyclopropylidene (**2**) when heated to 60°C, but rather underwent homodimerization to yield **15** (56%, E/Z = 1.3:1). The assignment of the two diastereomers was secured by an X-ray structure analysis of (E)-**15**.[11b]

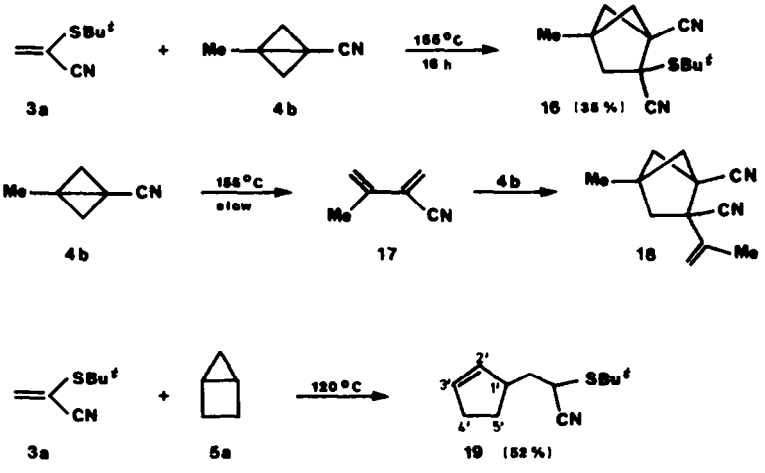
Additions of capto-dative olefins to **4** and **5**.

Whereas unsubstituted bicyclo[1.1.0]butane (**4a**) rearranges to 1,3-butadiene and cyclobutene between 125 and 135°C, 3-methylbicyclo[1.1.0]-butan-1-carbonitrile (**4b**) has been reported to react with various olefinic and acetylenic compounds via a radical mechanism at higher temperatures.[8] Therefore **4b** was chosen to react with capto-dative **3a** at 155°C. It did indeed give a 35% yield of the cyclo-adduct across the central single bond, 4-methyl-2-tert-butylthiobicyclo[2.-1.1]hexan-1,2-dicarbonitrile (**16**). Under the same conditions, **3c** and **3d** did not cycloadd to **4b**, but the only product isolated was **18**, a formal dimer of **4b** formed with the diene **17**.

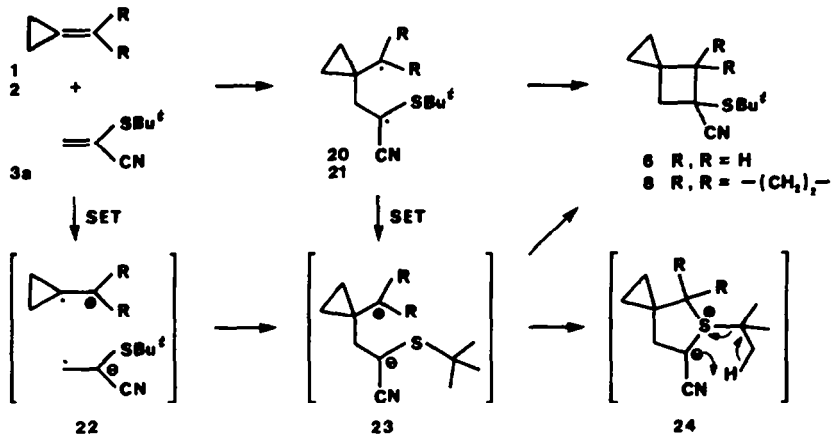
reacted with capto-dative **3a** at 120°C to give as the only isolable product the cyclopentene derivative **19** (52%) arising from a hydrogen shift in the intermediate diradical.

DISCUSSION

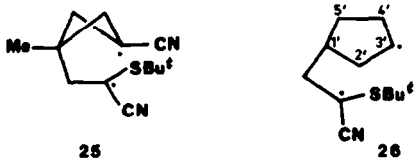
Whereas **1** and **2** cyclodimerize at temperatures between 200 and 250°C, some representatives of **3** form cyclo-butane derivatives even at room temperature, e.g. **3a** and the naturally occurring protonanemonine.[5] A number of these capto-dative olefins **3** have been found to readily undergo [2+2] cycloadditions with fluoroolefins and allenes[12] as well as [2+4] reactions with dienes and 1,3-dipoles.[13] The two types of products obtained from **1** and **2** with **3a** can both be rationalized to arise from the diradical intermediates **20** and **21**, respectively. While cycli-zation leads to the head-to-head cyclo-butanes **6** and **8**, single electron transfer (SET)[14] may compete to yield the zwitterion **23** which would prefer to cyclize across the more nucleophilic sulfur to give **24** and by concomitant



Bicyclo[2.1.0]pentane (**5a**) is known to react with various cyclophiles across its central single bond to give bicyclic along with monocyclic products via diradical intermediates.[7,8] The product distribution depends on the type of the cyclophile and thereby on the stability of the intermediate. **5a** loss of isobutene lead to **7** and **9**, respectively. Alternatively SET between **1**(**2**) and **3a** might occur first to give the radical ion pair **22** which would combine to the zwitterion **23**, com-peting cyclizations of the ambident nucleophilic end of **23** could then lead to **6**(**8**) and via **24** to **7**/**9**.



It is consistent with the general chemical behavior of both **4a**[8] and **3a**[4,5] that only one regioisomer **16** is formed most probably via the more stable 1,5-diradical **25**. The analogous diradical **26** formed from **5a** and **3a** apparently has no tendency to cyclize, but prefers to undergo an intramolecular disproportionation by γ-hydrogen abstraction as reported earlier for such 1,5-diradical intermediates.[7]



EXPERIMENTAL PART

General remarks. Melting points (uncorrected) were determined with a melting point apparatus by Wagner & Munz, Munich. - ^{1}H NMR: Bruker WM 270, WM 400, Varian XL 200; δ = 0 for tetramethylsilane, δ = 7.16 for benzene (C_6D_5H), δ = 7.26 for chloroform. - ^{13}C NMR: Bruker WM 400 (100.62 MHz), Varian CST 20; δ = 0 for tetramethylsilane, δ = 77.0 for chloroform, δ = 128.0 for benzene. - IR: Perkin-Elmer 297, 399. - MS: Varian MAT 311. - GC/MS: Varian MAT 112 with Varian Aerograph 1400. - GC (analytical): Siemens L 402, Siemens Sichromat 3 and Hewlett-Packard 5710 A; GC (preparative): Varian Aerograph 920.

Reaction of methylenecyclopropane (**1**) with 2-tert-butylthioacrylonitrile (**3a**): A mixture of 105 mg (1.9 mmol) **1** and 150 mg (1.06 mmol) **3a** in a sealed NMR tube was heated to 150°C for 24h, when the reaction was found to be complete. The mixture was separated by column chromatography over silica gel ($CHCl_3$/petrol ether (1:4)) to give 3 fractions:

I: mixture of **1** and **3a**.

II: 41 mg (20%) 5-tert-butylthiospiro-[2.3]hexan-5-carbonitrile (**6**), colourless oil. - IR (film): 3080, 3050, 2985, 2940, 2880, 2240, 1370, 1165 cm^{-1}. - ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 0.50 and 0.67 (2m, 2H, part of AA'BB'-system). - MS (70eV, m/z, %): 195(M^+,4), 172(M-CH_3,10), 138(M-C_4H_9, 14), 106(M-SC_4H_9,10), 85 (100), 58(91), 57(57), 42(40).

III: 37 mg (25%) 5-thiaspiro[2.4]-heptan-6-carbonitrile (**7**), colourless oil. - IR (film): 3080, 3050, 3000, 2940, 2860, 2240, 1425, 1225 cm^{-1}. - ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 0.70-0.81 (m, 3H, cyclopropyl-C$\underline{H}_2$), 0.90(m, 1H, cyclopropyl-C$\underline{H}$), 2.05(dd, 1H, J_{cis} = 4.3, J_{gem} = 12.7 Hz, C$\underline{H}_2$),

2.27(dd, 1H, J_{trans} = 6.8 Hz, J_{gem} = 12.7 Hz, $C\underline{H}_2$), 2.85(d, 1H, J_{gem} = 10 Hz, $C\underline{H}_2$), 2.96(d, 1H, J_{gem} = 10 Hz, $C\underline{H}_2$), 4.04(dd, 1H, J_{trans} = 6.8 Hz, J_{cis} = 4.3 Hz, $C\underline{H}_2$). - MS (70eV, m/z, %): 139(M^+,19), 124(M-CH_3,7), 111(M-C_2H_4,27), 86(M-C_4H_5,76), 67(100), 53(23), 45(23).

Reaction of bicyclopropylidene (**2**) with **3a**: A mixture of 130 mg (1.6 mmol) **2** and 147 mg (1.04 mmol) **3a** in a sealed NMR tube was heated to 100°C for 40 h, when the reaction was found to be complete. 213 mg of the crude reaction mixture were separated by preparative gas chromatography (1.3 m 10% SE 30, 130°C) to give 3 fractions:

I (rel. retention time 1.0): 60.5 mg mixture of **2** and **3a** (1:2.7).

II (12.7): 26.9 mg (24%) 7-thiadispiro-[2.0.2.3]nonan-8-carbonitrile (**9**), colourless oil. - IR (film): 3080, 3000, 2920, 2858, 2230, 1420, 1030 cm^{-1}. - ^1H NMR (400 MHz, C_6D_6, δ, ppm): -0.23(mc, 1H, cyclopropyl-$C\underline{H}_2$), -0.10 (mc, 1H, cyclopropyl-$C\underline{H}_2$), 0.05(mc, 3H, cyclopropyl-$C\underline{H}_2$), 0.28(mc, 2H, cyclopropyl-$C\underline{H}_2$), 0.40(mc, 1H, cyclopropyl-$C\underline{H}_2$), 1.51(2H, AB-part of ABX-system), 3.31(1H, X-part of ABX-system). - MS (70ev, m/z, %): 165(M^+,100), 150(M-CH_3, 97), 137(M-C_2H_4,40), 122(M-SH,40), 111(M-C_3H_4N,29), 97(57), 84($C_3H_2NS^+$, 50), 79($C_6H_7^+$,70). (Found: C, 65.53; H, 6.94; N, 8.23; S, 19.54. Calc for $C_9H_{11}NS$ (165.26): C, 65.41; H, 6.71; N, 8.40; S, 19.40.)

III (21.7): 51 mg (34%) 8-tert-butyl-thiodispiro[2.0.2.2]octan-8-carbonitrile (**8**), m.p. 43°C. - IR (film): 3070, 2990, 2960, 2940, 2900, 2860, 2225, 1475, 1460, 1425, 1365, 1155, 1020, 1005, 970 cm^{-1}. - ^1H NMR (400 MHz, C_6D_6, δ, ppm): -0.03-0.6(m, 6H, cyclopropyl-$C\underline{H}_2$), 0.84(mc, 1H, cyclopropyl-$C\underline{H}_2$), 0.95(mc, 1H, cyclopropyl-$C\underline{H}_2$), 1.32(s, 9H, $C(C\underline{H}_3)_3$), 2.60(AB, ν_A = 2.47, ν_B = 2.73, J = 8 Hz, 2H, $C\underline{H}_2$). - MS (70eV, m/z, %): 221(M^+,2), 206(M-CH_3,3), 193(M-C_2H_4,4), 164(M-C_4H_9, 23), 136(M-C_6H_{13},19), 132(M-C_4H_9S, 15), 80 (21), 57($C_4H_9^+$,100). (Found: C, 70.20; H, 8.65; N, 6.47; S, 14.62. Found: C, 70.07; H, 8.58; N, 6.37; S, 14.58. Calc. for $C_{13}H_{19}NS$ (221.37): C, 70.54; H, 8.65; N, 6.33; S, 14.49.)

Yields are based on reacted **3a** (85%), according to an analytical Gc the ratio of **8** to **9** was 3:1.

Reaction of bicyclopropylidene (**2**) with 2-methoxyacrylonitrile (**3c**): A mixture of 135 mg (1.69 mmol) **2** and 141 mg (1.69 mmol) 2-methoxyacrylonitrile (**3c**) was heated in a sealed NMR tube to 100°C for 24 h and 130°C for 4 d, after which the starting material **2** had completely disappeared. The reaction mixture was chromatographed with diethyl ether over 9 g silica gel (2.5 x 4 cm column) and the crude product purified by preparative gas chromatography (1.2 m 10% SE 30, 100°C) to yield 163 mg (59%) 2-methoxy dispiro[2.0.2.2]octancarbonitrile (**10**) as a colourless oil. - IR (film): 3070, 3000, 2940, 2230, 1740, 1460, 1420, 1260, 1210, 1120, 1080, 1030, 895 cm^{-1}. - ^1H NMR (270 MHz, $CDCl_3$, δ, ppm): 0.22(mc, 1H, cyclopropyl-$C\underline{H}_2$), 0.39(mc, 4H, cyclopropyl-$C\underline{H}_2$), 0.53(mc, 1H, cyclopropyl-$C\underline{H}_2$), 0.76(mc, 1H, cyclopropyl-$C\underline{H}_2$), 0.99(mc, 1H, cyclopropyl-$C\underline{H}_2$), 2.63(AB, ν_A = 2.56, ν_B = 2.69, J = 12 Hz, 2H, $C\underline{H}_2$), 3.37(s, 3H, $C\underline{H}_3$). (Found: C, 73.14; H, 7.89; N, 8.54. Found: C, 73.07; H, 7.89; N, 8.53. Calc. for $C_{10}H_{13}NO$ (163.22): C, 73.59; H, 8.03; N, 8.58.)

Reaction of methyl α-chloro-α-cyclopropylidene acetate (**11**) with 2-tert-butylthioacrylonitrile (**3a**): A mixture of 163 mg (1.11 mmol) **11** and 147 mg (1.04 mmol) **3a** in a sealed NMR tube was heated to 100°C for 40 h. 173 mg (56%) of the crude reaction mixture were separated by preparative thin-layer (2 mm) chromatography on silica gel with ether/petroleum ether (60/80) (1:5) and yielded 3 fractions:

I (R_F = 0.61): 61 mg (35%) educts **3a** and **11** (ratio 1:1.5).
II (R_F = 0.39): 105 mg (63%) 2.2:1.0 (^{1}H NMR) mixture of methyl-5-*tert*-butylthio-4-chloro-5-cyano-spiro[2.3]-hexan-4-carboxylate (**13**) and methyl-6-*tert*-butylthio-4-chloro-6-cyano-spiro[2.3]hexan-4-carboxylate (**14**). - IR (film): 2960, 2950, 2860, 2240 (C≡N, very weak), 1740 (C=O), 1455, 1430, 1360, 1280, 1250, 1165, 1100, 1050, 1030 cm^{-1}. - ^{1}H NMR (270 MHz, C_6D_6, δ, ppm): 69% fraction of isomer **15**: 0.20-0.34(m,3H, cyclopropyl-CH_2), 0.85-0.97(m, 1H, cyclopropyl-CH_2), 1.42(s, 9H, C(CH_3)$_3$), 2.32(AB, ν_A = 2.17, ν_B = 2.46, J = 11 Hz, 2H, CH_2), 3.27(s, 3H, CH_3); 31% fraction of isomer **16**: 0.20-0.34(m, 3H, cyclopropyl-CH_2), 0.85-0.97(m, 1H, cyclopropyl-CH_2), 1.40(s, 9H, C(CH_3)$_3$), 2.38(AB, ν_A = 1.99, ν_B = 2.77, J = 11 Hz, 2H, CH_2), 3.36(s, 3H, CH_3). - ^{13}C NMR (100.62 MHz, C_6D_6, δ, ppm): 9.61(cyclopropyl-CH_2), 11.06(cyclopropyl CH_2), 13.89(cyclopropyl-CH_2), 14.44(cyclopropyl-CH_2), 27.95, 28.17, 30.15, 31.66(C(CH_3)$_3$), 31.72 (C(CH_3)$_3$), 42.63(cyclobutane-CH_2), 43.22(cyclobutane-CH_2), 45.50, 47.93, 52.49(OCH_3), 52.56(OCH_3), 65.84, 79.76, 119.05(CN), 120.46(CN), 166.36(CO_2CH_3), 166.72 (CO_2CH_3). - MS (70eV, m/z, %): 287(M^+, 0.6), 272(M- CH_3,0.2), 231(M-C_4H_6,32), 196 (M-C_4H_9Cl,12), 164(M-C_4H_9SCl,8), 146($C_4H_7ClO_2^+$,6), 136 ($C_7H_6NS^+$,4), 115($C_6H_{11}S^+$,3), 111($C_6H_7O_2^+$,5), 57 ($C_4H_9^+$,100). (Found: C, 54.76; H, 6.36; N, 5.16; S, 10.92. Found: C, 54.67; H, 6.57; N, 4.99. Calc. for $C_{13}H_{18}NClO_2S$ (287.81): C, 54.25; H, 6.30; N, 4.87; S, 11.14.)

Reaction of methyl α-phenylthio-α-cyclopropylidene acetate(**12**) with **2**: A solutuion of 44 mg (0.20 mmol) **12** and 18 mg (0.23 mmol) **2** in 0.30 ml 1.4-dioxane was heated in a sealed NMR tube to 60°C for 9 h. The reaction mixture was chromatographed over 20 g silica gel (pentane/diethyl ether = 10:1) and yielded 2 fractions:
I (R_F = 0.21): 11 mg(25%) (Z)-**15**. - ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): 0.14-0.39(AA'BB', 4H, cyclopropyl-CH_2), 0.88-1.16(AA'BB', 4H, cyclopropyl-CH_2), 3.47(s, 6H, OCH_3), 7.24 and 7.50(m, 10H, C_6H_5). - MS (70 eV, m/z, %): 440(M^+,1.2), 363(M-C_6H_5,33), 331(M-SC_6H_5,100).
II(R_F = 0.25): 14 mg (31%) (E)-**15**. - ^{1}H NMR (270 MHz, $CDCl_3$, δ, ppm): -0.06(m, 2H, cyclopropyl- CH_2), 0.32(m, 2H, cyclopropyl-CH_2), 0.41(m, 2H, cyclopropyl-CH_2), 1.23(m, 2H, cyclopropyl-CH_2), 3.50(s, 6H, OCH_3), 7.23 and 7.50(m, 10H, C_6H_5). - MS (70eV, m/z, %): 440(M^+,1.1), 363(M-C_6H_5,33), 331(M-SC_6H_5,100).
The structure of (E)-**15** was confirmed by X-ray crystallography.

Reaction of 3-methylbicyclo[1.1.0]-butane carbonitrile (**4b**) with **3a**: A mixture of 1.0 g (10.7 mmol) **4b** and 1.5 g (10.7 mmol) **3a** in a sealed tube was heated to 155°C for 16 h. The mixture was separated by column chromatography ($CHCl_3$ over silica gel), and the product sublimed at 120°C (0.4 mm Hg); yield 0.86 g (35%) 4-methyl-2-*tert*-butylthiobicyclo[2.1.1.]hexan-1,2-dicarbonitrile (**16**), white crystals, m.p.80-82°C. - IR (film): 2960, 2925, 2875, 2240, 1460, 1370, 1160, cm^{-1}. - ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.24(s, 3H, CH_3), 1.58(s, 9H, C(CH_3)$_3$), 2.00(dd, 1H, J_{gem} = 6.9 Hz, ^4J = 2.8 Hz), 2.07-2.14(m, 2H), 2.17(m, 1H, J_{gem} ≈6.9 Hz), 2.20(m, 1H, cis to SR, J_{gem} ≈11.7), 2.51(dd, 1H, cis to CN, J_{gem} = 11.7, ^4J = 2.8). - ^{13}C NMR (200 MHz, $CDCl_3$, δ, ppm): 17.8(q, ^1J = 126 Hz, CH_3), 31.8(qm, ^1J = 127 Hz, C(CH_3)$_3$), 44.68(sm, C-CN), 46.21(tm, ^1J = 146 Hz, CH_2), 47.0(sm), 47.91(tm, ^1J = 145 Hz, CH_2), 48.32(sm, C(CH_3)$_3$), 51.47(tm, ^1J = 138 Hz, CH_2, gem. to C(CN)SR), 116.82(st, J≤1Hz, CN), 120.39(sm, CN). - MS (70 eV, m/z ,%): 234(M^+,3), 178(M-C_4H_8,6), 142(5), 57($C_4H_9^+$,100), 41(57).
The structure of **16** was confirmed by X-ray crystallography.[15]

Reaction of bicyclopentane(**5a**) with **3a**: A mixture of 0.8 g(11.7 mmol) **5a** and 1.7 g(12 mmol) **3a** in a sealed tube was heated to 120°C for 48 h. The reaction mixture was separated by column chromatography (CH_2Cl_2/ethyl acetate (1:1) over silica gel) to give, as the only isolable product, 1.27 g (52%) of a mixture of 3-(2'-cyclopentenyl)-1-tert-butylthiopropionitrile (**19**) and an unidentified isomer. - IR (film): 3050, 2960, 2860, 2240, 1613, 1160, 1020 cm^{-1}. - ^1H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.44(s, 9H, $C(CH_3)_3$), 1.7-2.2(m,4H), 2.33-2.38(m, 2H, allylic CH_2), 2.95-3.00(m, 1H, allylic CH), 3.45 and 3.47(m, 1H), 5.66 and 5.69(m, 1H, vinylic CH), 5.80 and 5.82(m, 1H, vinylic CH). - MS (70eV, m/z, %): 209(M^+,3), 153(M-C_4H_8,12), 119(M-C_4H_9S,15), 81($C_6H_9^+$, 18), 67(24), 57(100), 41(50).

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