83. Captodative Olefins in Normal and Inverse *Diels-Alder* Reactions[1])

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(9.XI.87)

Olefins with captodative substitution are reactive dienophiles in *Diels-Alder* reactions with normal and inverse electron demand. This is shown for reactions of 2-(*tert*-butylthio)acrylonitrile (**1**) with various dienes and heterodienes, *e.g.* 1,3-cyclohexadiene, hexachloro-1,3-cyclopentadiene, acrolein, methacrolein, and methyl vinyl ketone (*Schemes 2* and *3*). In case of the heterodienes, 3,4-dihydro-2*H*-pyrans are formed beside small amounts of tetrahydrothiophenes; however, with methyl vinyl ketone, both reaction pathways are equally followed. The high reactivity of captodative olefins in *Diels-Alder* reactions are rationalized on the basis of *Sustmann*'s FMO model under consideration of *Viehe*'s concept of captodative substitution of alkenes.

Introduction. – Among the important methods in organic synthesis particularly the *Diels-Alder* reaction holds an outstanding position [2] [3]. Its scope of application, however, is limited by one of the fundamental rules of thermal [4 + 2] cycloadditions: namely, a sufficiently high reaction rate is only achieved, if the frontier orbitals of the starting materials (HOMO and LUMO) are energetically close [2] [4]. Such ideal conditions are not always fulfilled, and there has, therefore, been no lack of attempts to find improvements for *Diels-Alder* reactions that yield poor results. Examples include reactions under catalysis by *Lewis* acids [5], high-pressure conditions [6], and the exploitation of the hydrophobic effect for reactions in aqueous media [7]. In addition, the radical-cation catalysis has found various applications in recent times [8]. We now wish to report about a further possibility to increase the reactivity of *Diels-Alder* reactions which result from the model of frontier-orbital interaction (FMO model) [2] [4] and from *Viehe*'s concept of captodative (c, d) substitution of alkenes [9].

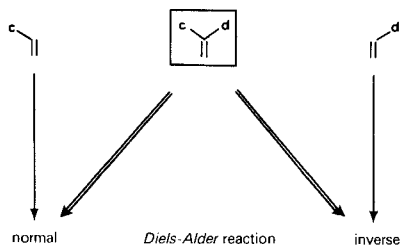
General. – According to *Sauer* and *Sustmann* [2] [4], high reactivities are only observed in *Diels-Alder* reactions, if either the HOMO (diene) and the LUMO (dienophile) are energetically close (normal, type I) or *vice versa* (inverse, type III). Numerous examples confirm this model[3]) which, in general, exclude each other [2]. Captodative (c, d) olefins which are defined by a geminate substitution with an electron acceptor (c) and an electron donor (d) group are characterized by relatively high HOMO and relatively low LUMO energies [9]. Therefore, these olefins should show increased interactions with

[1]) Part 3 of 'Thermal Reactions of Donor-Acceptor Systems'. Part 2: [1].

[2]) Taken in part from the diploma thesis (RWTH 1986) and from the planned Ph. D. thesis.

[3]) The interactions of both pairs of frontier orbitals have to be considered in the so-called neutral (type II) *Diels-Alder* reaction. Examples, however, are not frequent [2].

Scheme 1

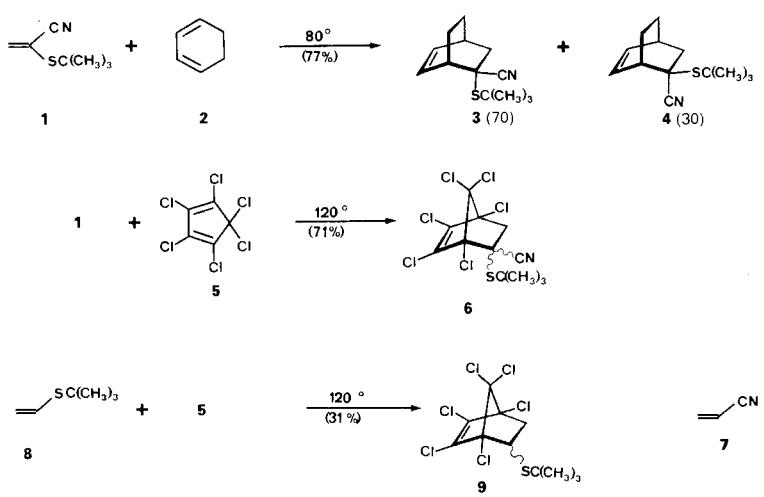


both electron-rich (type I) and electron-deficient dienes (type III) and consequently should be suitable for normal *and* inverse *Diels-Alder* reactions[4]) *(Scheme 1)*.

(c,d) Olefins have already been used in normal *Diels-Alder* reactions by *Stella* and coworkers [11]. Only very few examples have been reported concerning the inverse counterpart: *e.g. Takaki et al.* [12] found that 3-(phenylthio)-3-buten-2-one could be dimerized to 2-acetyl-2,5-bis(phenylthio)-6-methyl-3,4-dihydro-2*H*-pyran, and *Hünig* and coworkers reported about the cycloadditions of 2-(trimethylsiloxy)acrylonitrile with 1,3-cyclohexadiene and hexachloro-1,3-cyclopentadiene [13].

Results and Discussions. – The 2-[(*tert*-butyl)thio]acrylonitrile (**1**) [14] is a typical (c,d) olefin and forms *Diels-Alder* adducts in high yields with both 1,3-cyclohexadiene (**2**)[5]) and with the electron-deficient hexachloro-1,3-cyclopentadiene (**5**; see *Scheme 2*). In the former case, **3** with the *t*-BuS group in the *endo*-position is the main product besides **4**.

Scheme 2



[4]) Most recent results from *Rüchardt* and *Beckhaus* [10] which question the stabilization of radicals by (c,d) substitution ('merostabilization') obviously have no significance here, since the enhanced reactivity of (c,d) olefins in *Diels-Alder* reactions is caused by the smaller energetic distance of its HOMO and LUMO.

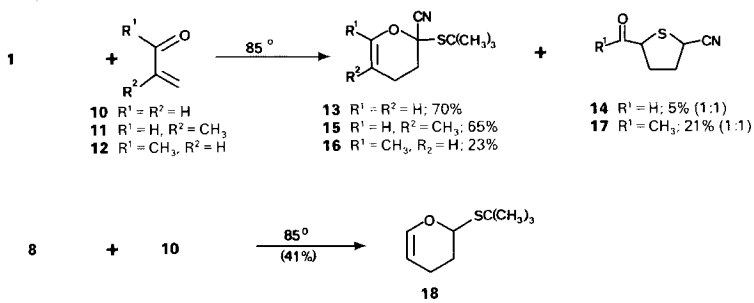
[5]) Similar results have been obtained with **1** and **2** in benzene at room temperature in presence of $AlCl_3$ as catalyst.

Similar observations have been made by *Stella* and *Boucher* [11] for reactions of 2-(methylthio)acrylonitrile with 1,3-cyclopentadiene and 1,3-cyclohexadiene. The configuration of **6** has not been assigned yet, since only one isomer is formed from **1** and **5** according to ^{13}C-NMR analysis.

Similar high reaction rates are only observed in cycloadditions between acrylonitrile (**7**) and **2** [15] (type I) and the thioenol ether **8** and **5** (type III; →**9**), respectively *(Scheme 2)*. Unfavourable pairs according to the *Sustmann* classification [2] [4] such as **7** + **5** and **8** + **2** either show only slow reaction rates [16] or do not react at all[6]). Further examples of type-I cycloadditions with (c, d) olefins have been reported by *Stella* and coworkers [11].

Our further investigations have been focussed on cycloadditions of **1** and α,β-unsaturated carbonyl compounds (see **10**–**12**). In general, these heterodienes only form *Diels-Alder* adducts efficiently with electron-rich dienophiles such as enol ethers [17], which corresponds to the *Sustmann*-type III. Normally the reaction temperatures are high [17] and may only be avoided by a further activation of the heterodiene [18] or under high-pressure conditions [19]. On the contrary, **1** and acrolein (**10**) form the 3,4-dihydro-2*H*-pyran **13** at 85° in 70% yield beside 5% of the 1:1 mixture of stereoisomeric tetrahydrothiophenes **14**. Further substitution of the acrolein unit by a Me group only changes the product ratios: whereas with 2-methylacrolein (**11**) almost exclusively[7]) the *Diels-Alder* cycloaddition to **15** has been observed, methyl vinyl ketone (**12**) forms both products **16** and **17** in nearly equal amounts (see *Scheme 3*). Compared to heterodiene syntheses with vinyl ethers, which generally require temperatures between 150 and 210° [17] or high pressure [6b], **1** is more reactive[5]) and in addition tolerates Me substituents at the enone unit as well.

Scheme 3



The *Diels-Alder* and the tetrahydrothiophene products are probably formed *via* two independent pathways, since the isolated products **13** and **14** from acrolein do not interconvert upon heating to 120°. The corresponding products from methyl vinyl ketone behave similarly, however, **16** slowly decomposes under these conditions. The thiophene derivatives may be formed *via* a mechanism which has already been described by *Döpp* and *Libera* [20] for reactions of **1** with maleic-acid derivatives. Here, however, we do not observe any stereoselectivity which might indicate a multistep mechanism.

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[6]) No formation of products from **8** and **2** has been observed under normal pressure at 80°.

[7]) The crude product contains two further 1:1 adducts (0.9 and 1.4%, resp.) according to GC/MS analyses.

For comparison, an equimolar mixture of **1**, **8**, and **10** was heated at 80°. At low conversion[8]), **13** and **18** were formed in equal amounts indicating same reactivities of the (c,d) olefin **1** and the thioenol ether **8** in the reaction with acrolein (**10**). This result shows that electronic properties such as the ionization potentials of the starting materials cannot be used alone for rationalizing the reactivities, since the corresponding parameters of **1** and **8** differ by 1 eV (see *Table*). As mentioned above, the FMO interactions have to be considered on the whole, which has also been shown by a recent kinetic analysis of the cycloadditions between 1-phenyl-4-benzylidene-5-pyrazolone and ethoxyethenes by *Desimoni* and coworkers [21]. The electrochemical redox potentials may serve for a qualitative estimation, which in addition are easier to determine than the corresponding ionization potentials and the electron affinities. The corresponding parameters do not only indicate the higher reactivity of **1** compared to **7** and **8** but also point to its (c,d) character, since both the oxidation and the reduction potentials are closer than in case of **7** and **8** *(Table)*. The latter corresponds to closer HOMO and LUMO levels.

Table. *Half-Peak Potentials and Ionization Potentials of Ethylene and the Olefins* **1**, **7**, *and* **8**

Olefin	*I.P.* [eV]	$E^{Ox}_{1/2}$ [V]	$E^{Red}_{1/2}$ [V]
Ethylene	10.51[b])	2.90[b])	< –3[c])
1	9.07[d])	1.86	–2.25
7	10.73[e])	3.67[e])	–2.63[e])
8	8.07[f])	1.58/1.98	[g])

[a]) Cyclic voltametry: working electrode Pt, reference electrode $Ag/AgNO_3$, concentration 1 mM in MeCN, supporting electrolyte 0.1 M tetrabutylammonium tetrafluoroborate, scan speed 100 mV/s.
[b]) From [22].
[c]) Estimated from a 'linear free energy relationship', see [23].
[d]) From [20].
[e]) From [23].
[f]) From [24].
[g]) Exact value is unknown due to the limited scope of experimental measurement.

Structures of the Products. – The structures of the products have been assigned spectroscopically by means of ^{1}H-NMR, ^{13}C-NMR, MS, and IR measurements. In case of the two isomeric tetrahydrothiophenes **17**, the structures were also confirmed by determining the C–H assignments using 2D-NMR and by measuring the H,H coupling using the COSY technique. However, it was not possible to assign the relative configuration at C(2) and C(5). According to *Boucher* and *Stella* [11], the *exo*-carbonitrile **3** has a larger difference in the chemical shifts of the vinylic protons than *endo*-carbonitrile **4**.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We are grateful to Dr. *J. Runsink* for the NMR analyses of the products, and we further gratefully acknowledge contributions of GC and HPLC materials as well as basic chemicals from *Bayer AG* and *BASF*. *J. Mertes* thanks the State NW for a fellowship (Graduiertenförderung).

[8]) At higher conversion, **18** undergoes further reactions, probably rearrangements according to GC/MS analyses.

Experimental Part

1. *General.* All reactions were carried out under Ar with magnetic stirring. The olefin **1** was synthesized according to the method described in [14]. The 2-propenal (**10**; *Fluka*) was used without further purification, and 3-buten-2-one (**12**; *Fluka*) and 2-methyl-2-propenal (**11**; *Aldrich*) were distilled before use and stabilized with hydroquinone. Flash chromatography (FC): silica gel *60* (0.04–0.063 mm) from *Machery & Nagel*. HPLC: *Gilson 303* chromatograph and *Chromosorb Si 60* columns. GC: *Siemens Sichromat 3*, 25 m *HP Ultra 2*, 150° isothermal, flame ionization detector. IR spectra: *Perkin Elmer 377, Perkin Elmer 1700,* $\tilde{\nu}_{max}$ in cm^{-1}. ^{1}H-NMR: *Varian VXR 300* (300 MHz), TMS as internal standard. ^{13}C-NMR: *Varian VXR 300* (75 MHz), TMS as internal standard. MS: *Varian Mat 212,* 70 eV, 250°.

2. *Cycloadditions with 1,3-Cyclohexadiene* (**2**) *and Hexachloro-1,3-cyclopentadiene* (**5**). *2-[(*tert-*Butyl)thio]bicyclo[2.2.2]hex-5-ene-2-carbonitrile* (**3**/**4**). A mixture of 6.0 g (75 mmol) of **2** and 2.9 g (20 mmol) of 2-[(*tert*-butyl)thio]-acrylonitrile (**1**) was heated 10 h at 80°. After evaporation of the excess of **2**, the residue was distilled (3.4 g, 77%); **3**/**4** 7:3 by ^{1}H-NMR of the crude product. The isomers were separated by HPLC (3% AcOEt/hexane). IR (neat): 3060, 3030 (=CH); 2950, 2870 (CH); 2230 (C≡N); 1605 (C=C). MS: 211 (1, M^+), 165 (10), 132 (3), 104 (3), 86 (3), 81 (8), 80 (100), 79 (19), 78 (3), 77 (10), 65 (3), 59 (4), 57 (50), 51 (7), 41 (42).

*2-*exo-*Carbonitrile* **3**. ^{1}H-NMR ($CDCl_3$): 6.33 (*t*, *J* = 8.5, 1 H); 6.21 (*t*, *J* = 8.5, 1 H); 3.03 (*m*, 1 H); 2.64 (*m*, 1 H); 2.46–2.05 (*m*, 2 H); 1.80–1.26 (*m*, 4 H); 1.49 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 133.8 (=CH); 130.6 (=CH); 123.7 (CN); 47.6 (C); 43.8 (CH_2); 41.4 (C); 38.4 (CH); 31.9 (CH_3); 29.4 (CH); 23.3 (CH_2); 22.9 (CH_2).

*2-*endo-*Carbonitrile* **4**. ^{1}H-NMR ($CDCl_3$): 6.45 (*t*, *J* = 6.1, 1 H); 6.44 (*t*, *J* = 6.7, 1 H); 2.98 (*m*, 1 H); 2.63 (*m*, 1 H); 2.35–2.10 (*m*, 2 H); 1.66 (*dd*, *J* = 13.5, 1.98, 1 H); 1.55–1.44 (*m*, 1 H); 1.30–1.19 (*m*, 2 H); 1.51 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 136.2 (=CH); 132.6 (=CH); 124.4 (CN); 47.4 (C); 43.6 (CH_2); 42.6 (C); 38.0 (CH); 32.0 (CH_3); 29.4 (CH); 24.1 (CH_2); 19.1 (CH_2).

*2-[(*tert-*Butyl)thio]-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2-carbonitrile* (**6**). To 3.6 g (26 mmol) of **1**, 6.0 g (22 mmol) of **5** was added. The mixture was heated under Ar for 6 h at 120°, then 50 ml of pentane were added to the black soln. The brownish solid was collected and recrystallized from MeOH: 6.6 g (72.0%). M.p. 94°. IR (KBr): 2960, 2900, 2870 (CH); 2240 (C≡N); 1605 (C=C). ^{1}H-NMR ($CDCl_3$): 3.45 (*d*, *J* = 13.3, 1 H); 2.65 (*d*, *J* = 13.3, 1 H); 1.57 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 133.4 (C=C–Cl); 132.3 (C=C–Cl); 116.5 (CN); 101.0; 84.5; 77.3; 51.0; 50.6; 50.4; 31.7 (CH_3). MS: 417 (0.6), 415 (1.4), 413 (1.7, M^+), 411 (0.9), 361 (2), 359 (4), 357 (5), 355 (3), 324 (2), 323 (1), 322 (2), 321 (1), 320 (1), 239 (2), 237 (2), 86 (3), 85 (2), 84 (5), 58 (4), 57 (100), 49 (5).

3. *Cycloadditions with Heterodienes* **10**–**12**. Under N_2, 20 mmol of **1** and 40 mmol of the heterodiene were heated at 85°. The reaction was stopped when all of **1** was consumed or no further reaction was observed (GC). For workup, the mixtures were first filtered over SiO_2 in order to remove polymeric materials and then distilled and, if necessary, separated by means of HPLC of FC.

4. *Products of* **1** *and* **10**. FC with EtOAc/hexane 4:6.

*2-[(*tert-*Butyl)thio]-3,4-dihydro-2*H*-pyran-2-carbonitrile* (**13**). Yield 70%. Colourless oil. B.p. 80°/0.05 Torr. IR (neat): 3060 (=CH); 2995, 2965, 2930, 2900 (CH_2); 2240 (C≡N); 1660 (C=C–O–C); 1225 (C–O–C). ^{1}H-NMR ($CDCl_3$): 6.25 (*td*, *J* = 6.13, 1.7, 1 H); 4.97 (*m*, 1 H); 2.30–2.12 (*m*, 4 H); 1.54 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 139.7 (=CH); 118.4 (CN); 102.1 (=CH); 75.1 (C); 48.1 (C); 32.6 (C); 31.7 (CH_3); 17.1 (CH_2). MS: 197 (1, M^+), 141 (31), 112 (10), 108 (2), 98 (2), 97 (1), 86 (2), 85 (2), 80 (3), 57 (100), 41 (28).

5-Formyl-2,3,4,5-tetrahydrothiophene-2-carbonitrile (**14**). Yield 5%. Yellowish oil. The ratio 1:1 of isomers was determined by ^{1}H-NMR of the crude product mixture. No separation of the isomers was possible by HPLC (EtOAc/hexane 4:6). IR (neat): 2960, 2940, 2870 (CH_2); 2730 (CHO); 2240 (C≡N); 1720 (C=O). ^{1}H-NMR ($CDCl_3$): 9.42 (*d*, *J* = 3.84, 1 H, isomer A); 9.39 (*d*, *J* = 2.2, 1 H, isomer B); 4.15–3.94 (*m*, 2 H); 2.54–2.04 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 193.7; 193.3 (CHO); 118.7; 118.6 (CN); 55.4; 54.6 (CH); 35.1; 34.3 (CH_2); 33.8; 33.4 (CH); 29.1; 28.7 (CH_2). MS: 141 (13, M^+), 113 (11), 112 (49), 105 (3), 87 (5), 86 (6), 85 (100), 78 (5), 60 (5), 59 (11), 58 (9), 45 (30).

5. *Products of* **1** *with* **11**. *2-[(*tert-*Butyl)thio]-5-methyl-3,4-dihydro-2*H*-pyran-2-carbonitrile* (**15**). Yield 65%. Colourless oil. B.p. 75°/0.03 Torr. IR (neat): 3080 (=CH); 2970, 2930, 2900, 2880 (CH); 2240 (C≡N); 1680 (C=C–O–C); 1250 (C–O–C). ^{1}H-NMR ($CDCl_3$): 6.08 (br. *s*, 1 H); 2.3–2.08 (*m*, 4 H); 1.62 (br. *s*, 3 H); 1.53 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 134.4 (=C–O); 118.7 (CN); 110.3 (=C–CH_3); 74.7 (C); 48.0 (C); 32.8 (CH_2); 31.7 (CH_3); 22.7 (CH_2); 18.1 (CH_3). MS: 211 (3, M^+), 157 (2), 156 (4), 155 (46), 128 (3), 127 (4), 126 (26), 122 (5), 112 (3), 110 (2), 94 (7), 71 (6), 67 (2), 58 (4), 57 (100), 55 (2), 41 (22).

The GC (*HP Ultra 2,* 150° isothermal) shows 2 more peaks in *ca.* 2% yield, which are assigned to be 1:1 adducts according to GC/MS measurements.

6. *Products of* **1** *and* **12**. FC with EtOAc/hexane 4:6.

*2-[(*tert*-Butyl)thio]-6-methyl-3,4-dihydro-2*H*-pyran-2-carbonitrile* (**16**). Yield 23%. Colourless oil. IR (neat): 3060 (=CH); 2995, 2965, 2920, 2900 (CH); 2240 (CN); 1690 (C=C–O–C); 1240 (C–O–C). ^{1}H-NMR ($CDCl_3$): 4.72 (*m*, 1 H); 2.3–2.0 (*m*, 4 H); 1.78 (*td*, *J* = 3.0, 1.0, 3 H); 1.55 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 147.2 (=C–O); 118.5 (CN); 96.8 (=CH); 75.5 (C); 48.0 (C); 32.3 (CH_2); 31.8 (CH_3); 19.6 (CH_3); 17.8 (CH_2). MS: 211 (1, M^+), 155 (41), 122 (7), 113 (11), 112 (39), 85 (6), 80 (6), 71 (12), 57 (100), 43 (24), 41 (28).

5-Acetyl-2,3,4,5-tetrahydrothiophene-2-carbonitrile (**17**). Yield 21%. Isomeric ratio 1:1 (^{1}H-NMR) in the crude product mixture. Separation of the 2 isomers by HPLC (EtOAc/hexane 4:6). Colourless oil. IR (neat): 2970, 2950, 2870 (CH); 2240 (CN); 1715 (C=O); 1358 ($COCH_3$). MS: 155 (10, M^+), 112 (25), 111 (14), 86 (6), 85 (24), 60 (2), 59 (3), 58 (3), 45 (7), 44 (2), 43 (100).

Isomer A: ^{1}H-NMR ($CDCl_3$): 4.16 (*t*, *J* = 6.1, 2 H); 2.32–1.90 (*m*, 4 H); 2.27 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 203.3 (C=O); 119.3 (CN); 55.9 (CH); 35.0 (CH_2); 33.4 (CH); 30.7 (CH_2); 27.0 (CH_3).

Isomer B: ^{1}H-NMR ($CDCl_3$): 4.22 (*dd*, *J* = 6.9, 2.7, 1 H); 4.09 (*dd*, *J* = 6.8, 3.0, 1 H); 2.63 (*dddd*, *J* = 12.7, 5.0, 3.5, 2.5, 1 H); 2.43 (*ddt*, *J* = 12.5, 5.2, 3.3, 1 H); 2.26 (*dddd*, *J* = 12.5, 11.2, 6.7, 5.4, 1 H); 2.21 (*s*, 3 H); 2.12 (*dddd*, *J* = 12.7, 11.2, 6.9, 5.3, 1 H). ^{13}C-NMR ($CDCl_3$): 203.6 (C=O); 120.2 (CN); 55.4 (CH); 35.2 (CH_2); 34.4 (CH); 30.8 (CH_2); 28.1 (CH_3).

7. *5-[(*tert*-Butyl)thio]-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene* (**9**). At 120°, 2.32 g (20 mmol) of 2-[(*tert*-butyl)thio]ethene (**8**) and 5.46 g (20 mmol) of **5** were stirred for 6 h. Then the mixture was distilled and **18** collected at 115°/0.05 Torr and further purified by crystallization from MeOH (2.4 g, 30.8%). M.p. 51°. IR ($CDCl_3$): 2960, 2940, 2920, 2900, 2860 (CH); 1605 (C=C). ^{1}H-NMR ($CDCl_3$): 3.72 (*dd*, *J* = 8.5, 3.7, 1 H); 3.08 (*dd*, *J* = 13, 8.5, 1 H); 2.23 (*dd*, *J* = 13, 3.7, 1 H). ^{13}C-NMR ($CDCl_3$): 132.2 (=C–Cl); 130.8 (=C–Cl); 120.2; 82.6; 78.2; 49.5 (CH); 47.3 (CH_2); 44.5; 31.3 (CH_3). MS: 392 (0.1), 390 (0.2), 388 (0.2, M^+), 386 (0.1), 300 (1.4), 298 (4), 296 (6), 294 (4), 263 (1), 261 (2), 259 (1), 116 (3), 101 (2), 59 (1), 58 (4), 57 (100), 45 (2), 41 (8).

8. *2-[(*tert*-Butyl)thio]-3,4-dihydro-2*H*-pyran* (**18**). At 85°, 3.48 g (30 mmol) of **8** and 3.36 g (60 mmol) of **10** were heated for 30 h. Filtration through Al_2O_3 and evaporation of the filtrate gave 2.1 g (41%) of **18** as colourless oil. IR (neat): 3060 (=CH); 2960, 2930, 2900, 2880 (CH); 1650 (C=C); 1220 (C–O–C). ^{1}H-NMR ($CDCl_3$): 6.25 (*td*, *J* = 6.31, 1.8, 1 H); 5.44 (*t*, *J* = 5, 1 H); 4.8 (*m*, 1 H); 2.20–1.90 (*m*, 1 H); 1.41 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 141.5 (=CH); 101.2 (=CH); 77.8 (CH); 43.5 (C); 31.0 (CH_3); 28.4 (CH_2); 18.1 (CH_2). MS: 172 (26, M^+), 116 (18), 115 (13), 87 (23), 85 (13), 83 (20), 60 (9), 57 (100), 41 (22).

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