

CYCLOPENTANE RING FORMATION IN THE CYCLOADDITION REACTION OF
3-ALKENYL RADICALS TO RADICOPHILIC OLEFINS

Radomir N. Saičić and Živorad Čeković*

Department of Chemistry, Faculty of Sciences, University of Belgrade,
Studentski trg 16, P. O. Box 550, Belgrade, and Institut for Chemistry,
Technology and Metallurgy, 11001 Belgrade, Yugoslavia

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Abstract: Regioselective additions of 3-alkenyl radicals (10 and 20) to electron deficient olefinic bonds (7 and 17), followed by intramolecular 5-*exo*-cyclization and repeated addition to radicophilic double bonds were investigated and combined into a sequence of reactions for the preparation of cyclopentane derivatives (9 and 19). High regioselectivity of 3-alkenyl radical (10) addition to the electron deficient olefinic bond (7) as well as of 5-*exo*-cyclization of intermediary 5-hexenyl type radical (11), was achieved. The fate of intermediary cyclopentylmethyl radicals (22 and 27) depends on the nature of substituents attached to radical carbon. In case of alkyl groups (22), the nucleophilic reactivity of radical intermediates was increased and an intermolecular addition reaction occurred with the formation of a new C-C bond. However, in case of aryl groups, mesomeric stabilization of the radical (27) suppress the addition reaction to the radicophilic olefinic bond, even when the latter was used in excess, in these cases only hydrogen abstraction takes place.

Regioselective free radical additions to olefins were systematically investigated and their wide synthetic applications were everywhere reviewed.¹⁻⁷ The selectivity of this type of radical addition reactions depends on the structure and stability of the carbon centered radical species as well as on the structure of the unsaturated compounds used.^{3,8-10} The effect of substituents on the selectivity has been explained by the FMO theory.⁸ By appropriate selection of substituents and the functionality of both reactive species, a high regioselectivity in a sequence of several addition reactions can be achi-

eved under mild experimental conditions.¹¹⁻¹³ Synthetic value of this methodology was confirmed by the construction of many carbocyclic,^{1,2,4,14} heterocyclic^{1,4,15} and polycyclic molecules.¹⁶

The methodology of combining several addition reactions into a sequence of reactions can be realized in cases where low energy differences between the SOMO-LUMO and/or SOMO-HOMO are existing.^{3,8,17} A decrease in the SOMO-LUMO energy difference is achieved by increasing the nucleophilicity of the radical species, and/or by attaching an electron-withdrawing substituent to the olefinic carbon increasing thus the electrophilicity of double bond.^{8,17,18} However, the attachment of an electron-withdrawing substituent to the radical carbon atom decreases the energy of the SOMO increasing thus the electrophilic properties of the radical; therefore in order to achieve the selectivity it is necessary to attach an electron-donating substituent to the olefinic carbon, which would reduce the difference of SOMO-HOMO and allow the selective interaction to become dominant.^{3,10,19}

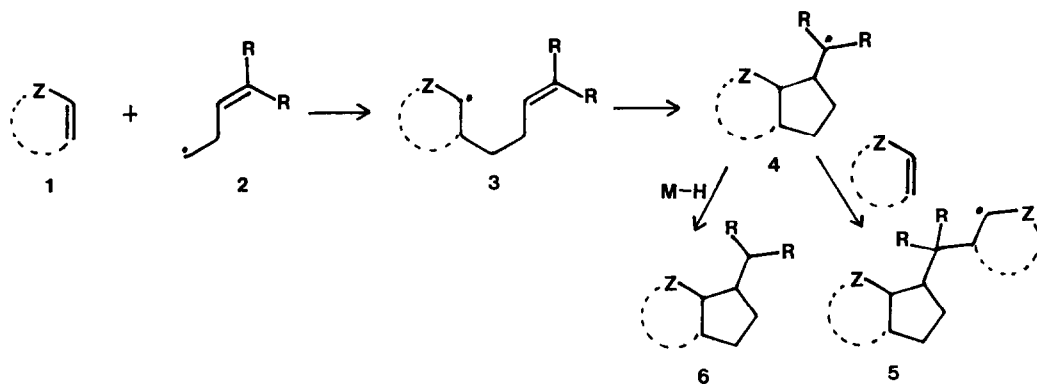
By adjusting the SOMO-LUMO as well as SOMO-HOMO interactions of several intermediary carbon radicals with olefinic bonds, the free radical intermediates can be "disciplined" to render possible the combination of several C-C bond forming addition reactions into one sequence of reactions.^{12,13,20,21}

In this paper we designed to realize a threefold (thribble) addition reaction by combining into a sequence of radical chain reactions (Scheme 1.):

i) Giese's intermolecular addition of 3-alkenyl radicals 2 to the electron deficient, radicophilic, olefinic compound 1,^{3,8} with ii) Walling-Beckwith's intramolecular 5-hexenyl radical 3 addition^{5,22,23} and iii) repeated Giese's addition of cycloalkylmethyl radical 4 to the olefinic compound 1. The proposed design offers a new approach to the preparation of polysubstituted cyclopentane derivatives starting from two different classes of unsaturated compounds, i.e. olefinic compounds having different coefficients of their frontier molecular orbitals.

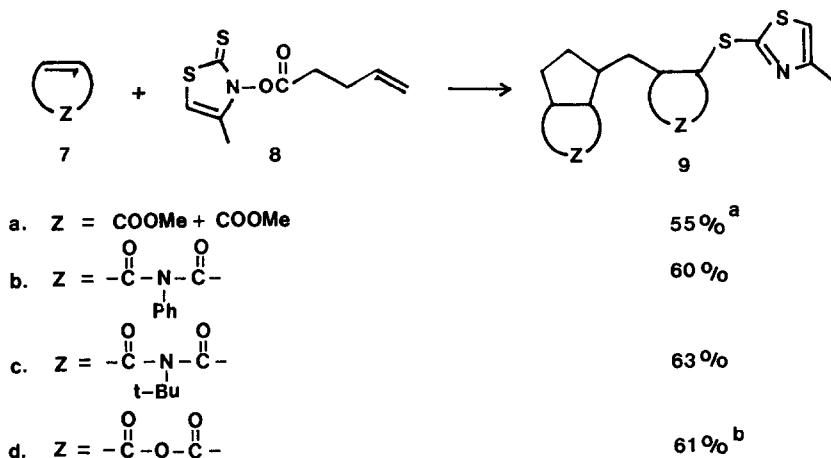
To achieve the sequence of regiocontrolled radical addition reactions for cyclopentane ring annulation shown in Scheme 1., the reactivity of all intermediary radical species should be brought in accord with the radicophilic properties of the olefinic bond.

When 3-butenyl radical, generated by thermal decomposition of thiohydroxamic ester of 4-pentenoic acid 8 (Barton's method²⁴), and a radicophilic olefinic compound (7a-7d) were used the regioselective threefold addition occurred affording polysubstituted cyclopentane derivatives 9 (Scheme 2.).



Scheme 1.

The decomposition of thiohydroxamic esters **8** was carried out under thermal conditions in boiling benzene or toluene, the reaction being initiated by AIBN.²⁴ The course of reaction was monitored by TLC.



^a The yields of compounds isolated by column chromatography

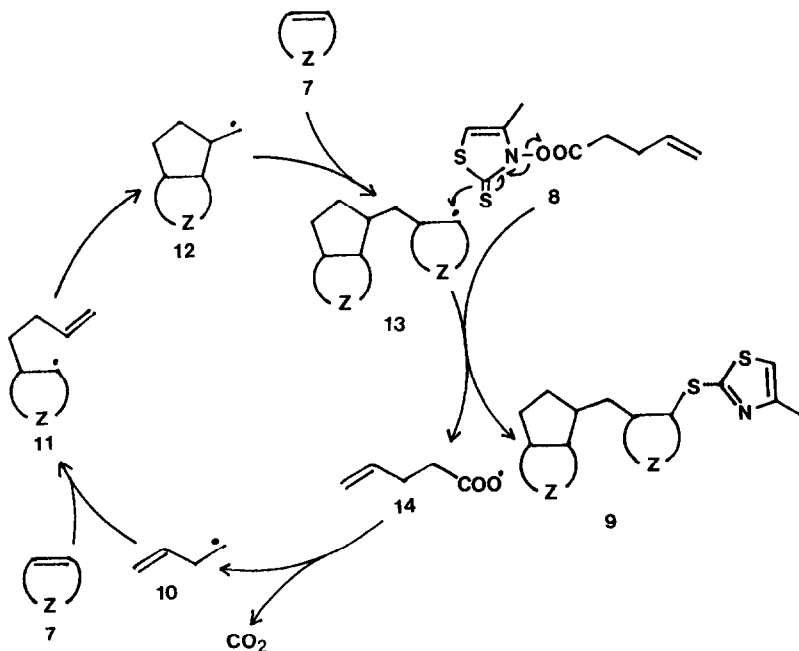
^b During the reaction elimination of 2-mercapto-4-methylthiazole occurs (see Scheme 4.)

Scheme 2.

The initially generated 3-butenyl radical **10** being enough nucleophilic undergoes an intermolecular addition to the radicophilic olefinic bond of maleic acid derivatives **7**, because its high energy SOMO interacting with low energy LUMO of electron deficient olefin.^{8,17} Since the rate constant of addition reaction of 3-butenyl radical **10** to the C=S bond of the star-

ting thiohydroxamic ester 8 and the rate constant of intermolecular addition to the radicophilic olefin 7 are almost the same ($10^6 \text{ M}^{-1} \text{ s}^{-1}$)^{8,25} in order to increase the relative rate of C-C bond formation we used an excess of three equivalents of electron deficient olefinic compounds 7 (Scheme 3.). When equal amounts of starting thiohydroxamic ester 8 and olefinic compounds 7 were used the cyclopentylmethyl radical 12 as well as 3-butenyl radical 10 attack rather the C=S bond of starting ester 2 instead of undergoing an intermolecular addition to the olefinic compound 7. Under these conditions the yields of cyclopentane derivatives 9 were considerably decreased, while the formation of the corresponding thioethers was favoured.

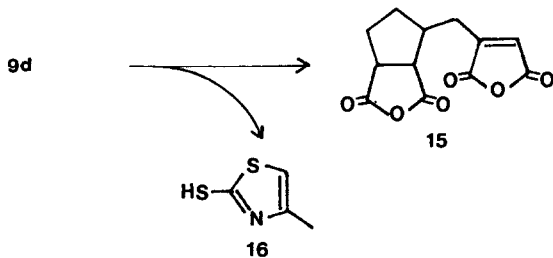
The newly generated radical 11 (Scheme 3.) having an electron-withdrawing substituent at the radical carbon has electrophilic character and low energy SOMO; it reacts internally with high energy HOMO of the olefinic bond in the 5-position and generates the cyclopentylmethyl radical 12 with high energy SOMO. In the latter cyclization reaction an inversion of the reactivity of radical species occurs, since an electrophilic radical 11 gives rise to a nucleophilic radical 12. The carbon centered radical 11, possessing electrophilic properties cannot react with an electron deficient olefinic bond even when a high concentration of 7 was used.



Scheme 3.

In the next step of this radical chain reaction the cyclopentylmethyl radical 12, being enough nucleophilic, reacts with radicophilic olefinic bond of compound 7, generating thus again an electrophilic radical species 13 which has low energy SOMO. Carbon radical of type 13, as that of radical type 11, cannot react with low energy LUMO of electron deficient olefinic bond, but, its lifetime permits its addition to the C=S bond of the starting thiohydroxamic ester,²⁶ inducing thus the decarboxylation of ester 8, i.e. 4-pentenoyloxy radical 14, and generation of a new 3-butenyl radical 10.

When maleic anhydride 7d was used as the olefinic radical acceptor and the reaction was carried out in boiling toluene (about 115°C), instead of compound of type 9, the unsaturated compound 15 was obtained (Scheme 4.). The latter was formed by thermally induced elimination of 2-mercapto-4-methylthiazole 16 from 9d. Since the corresponding saturated compound was not dete-



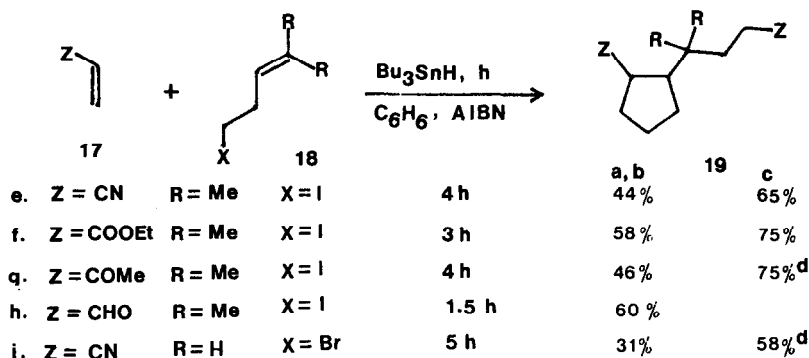
Scheme 4.

cted, the formation of the unsaturated product 15 cannot be assumed to proceed by disproportionation of the intermediary radical of type 13 (Scheme 3.).

In order to check the synthetic value of the proposed threefold (thribble) addition reaction which gives rise to the annulation of functionalized cyclopentane ring, the initially 3-alkenyl radicals were generated by tributyltin hydride (TBTH) reduction of the corresponding 3-alkenyl halides. The correlation of the reactivity and structure of the intermediary radicals in this chain cyclization reaction was also investigated.

When 3-alkenyl radical was generated by TBTH reduction of 3-alkenyl halides 18 in the presence of an excess of electron deficient, radicophilic, olefinic compounds 17 (AIBN as initiator and benzene as a solvent were used), the thribble addition reaction also took place and formally 3 + 2 cycloaddition occurred. High selectivity of three C-C bond formation reaction leading to cyclopentane ring 19 annulation was also observed.¹² The results obtained are summarized in Scheme 5.

In this sequence of reactions the radicophilic olefinic compounds 17 with



^a The yields of compounds isolated by column chromatography.

^b Mixtures of *cis*- and *trans*-isomers.

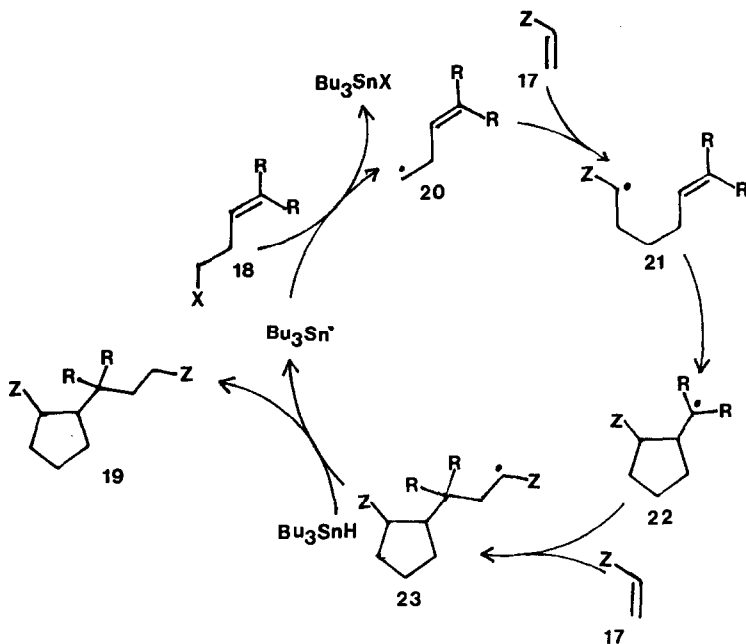
^c Gas chromatography yields.

^d Bu_3SnH was prepared *in situ* by Bu_3SnCl reduction with NaBH_4 in *t*-butanol.

Scheme 5.

only one electron-withdrawing group attached to the unsaturated carbon were used as acceptors of 3-alkenyl radicals.

The first step in this cycloaddition reaction is the generation of 3-alkenyl type radical 20 (Scheme 6.) which, in the presence of a tenfold excess of acrylonitrile or other radicophilic olefinic compound 17, undergoes an intermolecular addition rather than hydrogen abstraction from TBTH, although the rates of these two reactions are almost the same ($k_a \approx k_H \approx 10^6 \text{ M}^{-1} \text{ s}^{-1}$, at room temperature and equal molar ratio).⁸ The new arised 5-alkenyl type radical 21, possesses electrophilic properties and has low energy SOMO; it preferentially attacks the HOMO of the internal olefinic bond with the formation of a new carbon centered radical 22. When two methyl groups are attached to the tertiary cyclopentylmethyl radical 22 ($\text{R} = \text{CH}_3$) the following two competing reactions can be observed: hydrogen abstraction from TBTH and intermolecular addition to the electron deficient olefins (17).^{8,17} Since an excess of radicophilic olefin 17 used and possessing an increased nucleophilic reactivity radical species 22 undergoes to a third addition, i.e. the C-C bond formation reaction and hydrogen abstraction reaction was completely suppressed. The new generated electrophilic radical 23 have not appropriate LUMO for interaction, and abstracts rather the hydrogen from TBTH (Scheme 6.). In case 3-butenyl bromide 18i ($\text{R} = \text{H}$) was used as a precursor of 3-butenyl radical (20, $\text{R} = \text{H}$) the primary cyclopentylmethyl radical 22 also underwent the third addition rather than hydrogen abstraction reaction.



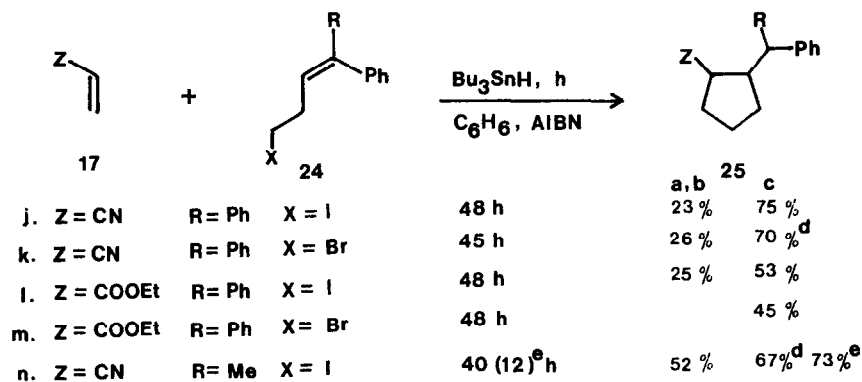
Scheme 6.

In addition to standard reaction conditions, reactions of alkenyl halides 18g and 18i were also carried out by preparing TBTH in situ by reducing tributyltin chloride with sodium borohydride. This experimental modification had no effect on yields of the products 19 (g and i) (Scheme 5.).

In both reactions described for cyclopentane ring annulation (Schemes 3. and 6.), the primary (12 and 22i) and tertiary cyclopentylmethyl radicals (22e-h) involved as intermediates displayed similar reactivities, in the presence of an excess of electron deficient olefinic compounds 17 both underwent the addition reaction rather than other stabilization reactions, regardless of the 3-alkenyl radical 20 precursor or experimental conditions applied.

The reactivity and selectivity of the intermediary cyclopentylmethyl radical was considerably changed by introducing some radical stabilizing groups in the δ -position of 3-alkenyl halides 18 which can stabilize the carbon radical of cyclopentylmethyl type, and in such a case the tandem addition only occurs. When one or two aryl groups are attached to the δ -carbon atom of 3-butenyl radical 20, 2-substituted cyclopentylmethyl derivatives 25 were obtained (Scheme 7.).

When 3-alkenyl type radical was generated by TBTH reduction of alkenyl halides of type 24 ($\text{R} = \text{Ph}$), the first addition reaction to the radicophilic



^aThe yields of compounds isolated by column chromatography.

^bMixture of *cis*- and *trans*-isomers.

^cGas chromatography yields.

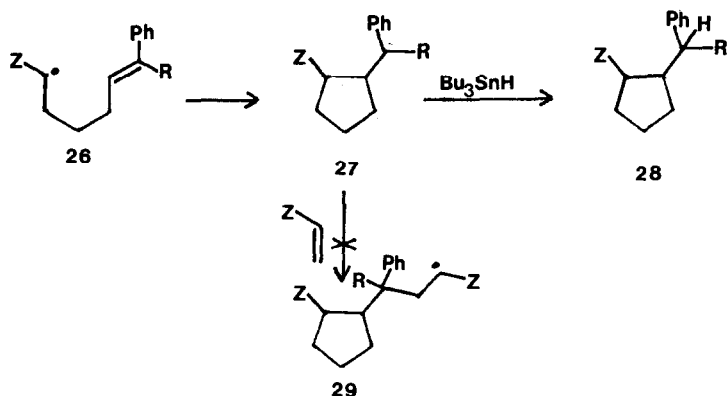
^dTBTH was prepared *in situ* by reduction of Bu_3SnCl with sodium bor hydride in *t*-butanol.

^eThe reaction was carried out with irradiation of reaction mixture at r.t. In addition to the cyclic product 25n the corresponding alkene was isolated in yield of 4%.

Scheme 7.

olefins 17 is the same as already described. The next intramolecular addition, from the standpoint of FMO theory, proceeds in a similar manner as already shown, and a cyclopentylmethyl radical of benzylic type 27 is generated (Scheme 8.). However, due to the presence of one or two phenyl groups at the radical carbon, the fate of radical 27 is changed with respect to that of radical 22 ($\text{R} = \text{CH}_3$). Phenyl group stabilize the carbon radical 27 by mesomeric effect decreasing thus the nucleophilic reactivity and the rate of addition to the olefinic bond similar to the polar effect of electron-withdrawing groups in radicals of type 26.^{3,8,17} Thus the benzylic type of cyclopentylmethyl radical 27 undergoes hydrogen abstraction reaction giving rise the cyclopentane derivative 28 rather than the intermolecular addition reaction to olefin 17 (Scheme 8.). The rate of intermolecular addition of stabilized radical 27 to the electron deficient olefinic bond 17 is much slower ($10^6 \text{ M}^{-1} \text{ s}^{-1}$) than is the rate of hydrogen abstraction. Namely, by decreasing the nucleophilic reactivity and the energy of SOMO of cyclopentylmethyl radical 27, and its reactivity with LUMO is decreased affording thus the corresponding 2-substituted cyclopentylmethyl derivatives 28.

The reaction of 3-alkenyl halides 24 with TBTH and olefinic compounds 17 proceeds considerably slower (40-48 hrs) than the reaction of 3-alkenyl halides 18 (1.5-4 hrs), under the same conditions applied. Since substitu-



Scheme 8.

ents at the δ -carbon atom of 3-alkenyl radical **20** do not influence the rates of reactions involved (reduction, inter- and intramolecular addition) we assume that the rate of hydrogen abstraction by stabilized cyclopentylmethyl radical **27** ($R = \text{Ph}$) from TBTH is the rate determining step.

When the reaction of 3-alkenyl halides with TBTH and acrylonitrile was carried out with irradiation of the reaction mixture, the reaction time was considerably shorter but the yield of cycloaddition product (**25n**) was unaffected (Scheme 7.).

From the results presented it can be seen that by appropriate selection of initial 3-alkenyl type radicals and unsaturated compounds with electron deficient olefinic bond, a rational design of a synthetic sequence of reactions for cyclopentane ring annulation can be achieved. Although the yields of polysubstituted cyclopentane derivatives obtained are not optimized, we believe that a new method for the construction of functionalized cyclopentane molecules, in one step, is on choice.

EXPERIMENTAL

Purification of starting materials and separations of the reaction products were carried out by column chromatography using silica-gel (0.063-0.200 mm), and/or by preparative gas chromatography on a Varian 920 instrument. Analytical gas chromatography was performed on a Varian GC-3400 instrument with a Varian 4270 integrator, using 5% OV-101 on Chromosorb WDMCS and 10% OV-275 on Chromosorb P columns. NMR spectra (ppm in δ -values) were recorded in CDCl_3 (if not otherwise stated) on a Varian FT 80-A spectrometer (^1H at 80 MHz and ^{13}C at 20 MHz); TMS was used as an internal standard. IR spectra (ν_{max} in cm^{-1}) were recorded on a Perkin Elmer 457 Grating instrument. Mass spectra were obtained on a Finnigan MAT 8230 instrument.

I. Decomposition of thiohydroxamic ester of 4-pentenoic acid 8.I.A. Synthesis of thiohydroxamic ester of 4-pentenoic acid 8.

N-Hydroxy-4-methylthiazol-2-thion (Thiohydroxamic acid)²⁴ - To a cooled (0°C) solution of 24.4 g (0.428 M) of KOH in 190 ml of water, a solution containing 15 g (0.078 M) of the oxime of S-acetyl-O-ethyl-dithiocarbonate (obtained from S-acetyl-O-ethyl-dithiocarbonate²⁷) in 190 ml of CH₂Cl₂ was added with stirring. The reaction mixture was then acidified with 4M HCl. The organic layer was separated and washed with water and saturated sodium chloride solution and dried (Na₂SO₄ anh.). Solvent was removed by evaporation under reduced pressure and the solid residue was crystallized from benzene. Pure thiohydroxamic acid, m.p. 93-94°C, was obtained in a 36% yield. ¹H-NMR: 2.40 (d, 3H, J = 1.5 Hz); 6.30 (q, 1H, J = 1.5 Hz); 8.50 (s broad, 1H).

Thiohydroxamic ester of 4-pentenoic acid 8. To a solution of 0.6 g (4.06 mM) of thiohydroxamic acid and 0.237 g (3.0 mM) of pyridine in 10 mL of toluene, a solution of 4-pentenoic acid (0.40 g, 3.38 mM) in toluene (5 ml) was added dropwise. The reaction mixture was stirred at r.t. for 1 h and then filtered off. A clear solution of thiohydroxamic ester of 4-pentenoic acid in toluene was obtained and it was used in the following reactions without isolation of the pure ester.

I.B. Decomposition of thiohydroxamic ester of 4-pentenoic acid 8 in the presence of electron deficient olefins. General method.

To a boiling solution of electron deficient olefinic compound (15 mM) in toluene (15 ml (argon was bubbled throughly during 10 min.)), a solution containing 0.75 g (5 mM) of thiohydroxamic ester in 25 ml of toluene was added dropwise during 15 min. in argon atmosphere. The reaction mixture was then refluxed for further 30 min., the course of reaction being monitored by TLC. Solvent was removed by evaporation under reduced pressure. The separation of the reaction products is carried out by chromatography on silica-gel column (benzene/ethyl acetate 8 : 2).

i) In the presence of dimethyl maleate 7a. In the reaction of thiohydroxamic ester of 4-pentenoic acid 8 (4.4 mM) with dimethyl maleate (13.3 mM) in the presence of catalytic amount of AIBN, the cyclopentane derivative 9a was obtained in a 55% yield. ¹H-NMR: 1.20-2.30 (m, 7H); 2.40 (s, 3H); 2.90-3.40 (m, 3H); 3.55-3.75 (ss, 12 H); 4.15-4.75 (m, 1H); 6.80 (s, 1H). Analysis: found: C, 50.10; H, 5.70; N, 2.55; S, 14.20%; C₁₉H₂₇O₈NS₂ requires: C, 49.35; H, 5.85; N, 3.03; S, 13.88%.

ii) In the presence of N-phenylmaleinimide 7b. The reaction of thiohydroxamic ester 8 with N-phenylmaleinimide afforded crystalline cyclopentane derivative 9b in 60% yield, m. p. 97-100°C. IR (KBr): 1710, 1600, 1500, 1380, 1190, 1040, 750, 695 cm⁻¹. ¹H-NMR: 1.20-2.70 (m, 10H, with s on 2.30); 3.97 and 4.40 (dd, J = 5 Hz, 1H, two stereoisomers); 6.80 (s, 1H); 7.10-7.60 (m, 10H).

iii) In the presence of N-t-butylmaleinimide 7c. The cyclopentane derivative 9c was obtained in 65% yield when decomposition of thiohydroxamic ester of 4-pentenoic acid 8 was carried out in the presence of three fold excess of N-t-butylmaleinimide. Analysis: found:

C, 56.70; H, 6.80; N, 9.20; S, 13.75%; $C_{23}H_{33}O_4N_3S_2$ requires: C, 57.62; H, 6.88; N, 8.76; S, 13.36%. 1H -NMR: 1.30-1.50 (ss, 18H); 1.50-2.50 (m, 10H, with s on 2.40); 2.75-3.40 (m, 3H); 3.15 (d, $J = 6$ Hz) and 3.85 (d, $J = 6$ Hz) 1H (cis- and trans-isomers on the second maleinimide ring); 6.15 (s, 1H).

iv) In the presence of maleinanhydride 7d. By decomposition of thiohydroxamic ester 8 (0.916 g, 4 mM) in the threefold excess of maleinanhydride (1.20 g, 12 mM), the unsaturated bicyclic product 15 was obtained in 62% yield. IR: 3120, 1850, 1750, 1240, 930, 895, 700 cm^{-1} . 1H -NMR: 1.25-3.00 (m, 7H); 3.10-3.70 (m, 2H); 6.87 (t, $J = 1.3$ Hz, 1H). Analysis: found: C, 57.50; H, 4.25%; $C_{12}H_{10}O_6$ requires: C, 57.60; H, 4.25%.

II. Reduction of 3-alkenyl halides by tributyltin hydride (TBTH) in the presence of electron deficient olefinic compounds

II.A. Synthesis of 3-alkenyl halides 18 and 24. Alkenyl halides 18 and 24 were prepared by cyclopropane ring opening of the corresponding tertiary cyclopropanemethanols by magnesium halides in an inert atmosphere.²⁸

4-Phenyl-3-penten-1-yl iodide 24n.²⁸ To a suspension of 5.35 g (0.22 gA) of magnesium in 350 ml of ether, 55.4 g (0.22 M) of iodine was added in a small portions in argon atmosphere. The reaction is exothermic. After iodine was added the reaction mixture refluxed for 0.5 h. Ethereal solution of magnesium iodide was filtered in argone atmosphere. To a clear ethereal solution of magnesium iodide, 17.8 g (0.11 M) of 1-phenyl-1-cyclopropylethanol dissolved in 50 ml of ether was added. The reaction mixture was refluxed and stirred in an inert atmosphere during 2.5 h. When reaction was completed the reaction mixture was washed with aqueous 10% solution of sodium thiosulfate and saturated sodium chloride solution. After drying (Na_2SO_4 anh.) ether was evaporated and residual oil was distilled under reduced pressure. 4-Phenyl-3-penten-1-yl iodide was collected at $132^{\circ}C/2$ mm Hg, 23.3 g (75% yield). 1H -NMR: 2.00 (s, 3H); 2.80 (q, 2H); 3.20 (t, 2H); 5.20 (t, 1H); 7.20-7.50 (m, 5H). Satisfactory IR spectra was obtained.

4,4-Diphenyl-3-buten-1-yl iodide 24j. According to the previously described procedure 4,4-diphenyl-3-buten-1-yl iodide was prepared from 3.93 g (17.5 mM) of diphenylcyclopropylmethanol. It was obtained 4.68 g (80%) of 4,4-diphenyl-3-buten-1-yl iodide, b.p. $172^{\circ}C/0.8$ mm Hg. 1H -NMR: 2.20 (q, 2H); 3.20 (t, 2H); 6.05 (t, 1H); 7.10-7.70 (m, 10H).

4,4-Diphenyl-3-buten-1-yl bromide 24k. To an ethereal solution of magnesium bromide, prepared from 3.9 g of magnesium and 22.5 g of 1,2-dibromoethane in ether, 7.5 g (33.25 mM) of diphenylcyclopropylmethanol, dissolved in 20 ml of ether, was slowly added. The reaction mixture was refluxed during 1 h, and worked up as described above. It was obtained 4.8 g (50%) of 4,4-diphenyl-3-buten-1-yl bromide, b.p. $158^{\circ}C/1$ mm Hg. 1H -NMR: 2.70 (q, 2H); 3.45 (t, 2H); 6.10 (t, 1H); 7.10-7.50 (m, 10H).

4-Methyl-3-penten-1-yl iodide 18e. Iodide 18e was prepared from 1-methyl-1-cyclopropylethanol (3.44 g, 34.4 mM) according to the described procedure. It was obtained 3.4 g (47%) of 4-methyl-3-penten-1-yl iodide, b.p. $29^{\circ}C/2$ mm Hg. 1H -NMR: 1.00 (s, 3H); 1.80 (s, 3H); 2.55 (q, 2H); 3.10 (t, 2H); 5.15 (t, 1H).

3-Buten-1-yl bromide 18i. This bromide was prepared according to the described procedure.²⁹

II.B. Reduction of 3-alkenyl halides 18 and 24 by TBTH. General procedure.

The solution of 1 mM of 3-alkenyl hydrides, 10 mM of electron deficient olefinic compounds, 1.1 mM of TBTH and catalytic amount of AIBN in 20 ml of benzene was heated to reflux in argon atmosphere. The course of reaction was monitored by TLC. When TBTH was completely consumed, an excess of electron deficient olefinic compounds and benzene were removed by distillation under reduced pressure. The residue was dissolved in ether and treated with a saturated aqueous solution of sodium fluoride (to remove tributyltin halide by precipitation as a tributyltin fluoride³⁰). Ethereal solution was dried by anhydrous Na_2SO_4 , ether was removed by evaporation under reduced pressure and residual mixture was analyzed by gas chromatography and separated by chromatography on silica-gel column.

Reductions were carried out under photolytical conditions (Hg-lamp) at room temperature in an ethereal solution.³¹ Almost the same yields of cyclization products were obtained, see Schemes 2 and 5, while reaction times were considerably shorter.

Similar results were obtained when TBTH was prepared in situ by using 0.4 mM of tributyltin chloride and 2.22 mM of sodium borohydride as a reducing agent. Catalytic amount of AIBN was also used. These reactions were carried out in *t*-butanol.³²

2-Cyano-1-(diphenylmethyl)-cyclopentane 25j ($Z = \text{CN}$, $R = \text{Ph}$). This cyclopentane derivative was obtained in 75% yield by TBTH reduction of 4,4-diphenyl-3-buten-1-yl iodide (24j) in acrylonitrile. IR: 3018, 2242, 1600, 1500, 1455, 750, 710 cm^{-1} . $^1\text{H-NMR}$: 1.10-2.20 (m, 7H); 2.80-3.00 (m, 1H); 4.00 (d, $J = 12$ Hz, 1H); 7.10-7.40 (m, 10H).

Cyclopentane derivative 25j was also obtained by modified procedure where TBTH was prepared in situ by using Bu_3SnCl (0.4 mM) and sodium borohydride (2.2 mM) and 4,4-diphenyl-3-buten-1-yl bromide as starting material. Reaction was carried out in *t*-butanol. Compound 25j was obtained in 70% yield.

Ethyl 2-(diphenylmethyl)cyclopentanecarboxylate 25l. By TBTH reduction of 4,4-diphenyl-3-buten-1-yl bromide (24m) in the presence of ethyl acrylate in excess the title compound 25l was obtained in 45% yield. However, by using the corresponding iodide 24l as precursor of 3-alkenyl radical, the cyclopentane derivative 25l was obtained in 53% yield. $^1\text{H-NMR}$: 1.20 (t, 3H); 1.40-2.00 (m, 7H); 2.20-3.90 (m, 2H); 4.10 (q, 2H); 7.10-7.40 (m, 10H). Analysis: found: C, 81.45; H, 7.90%; $\text{C}_{21}\text{H}_{24}\text{O}_2$ requires: C, 81.81; H, 7.79%.

2-(1-Phenylethyl)-cyclopentanecarbonitrile 25n. In the reaction of 4-phenyl-3-penten-1-yl iodide 24n (mixture of *Z* and *E* isomers was used) with acrylonitrile, according to the described procedure, the title compound was obtained in 67% yield as a mixture of *cis*- and *trans*-isomers. When the reaction was carried out under thermal conditions, in boiling benzene it was completed for 40 hrs; however, by running the reaction under irradiation conditions (Hg-lamp) at r.t. and using ether as solvent, the reaction time was only 12 hrs and the same yield of cyclic product 25 was obtained. IR: 3040, 2240, 1500, 1460, 770, 710 cm^{-1} . $^1\text{H-NMR}$:

1.35 (d, 3H); 1.40-2.25 (m, 7H); 2.60-3.20 (m, 2H); 7.10-7.30 (m, 5H). MS: M^+ 199 (9.5%), 115 (4.4%), 105 (100%), 91 (11.8%), 77 (9.5%).

4-(2-Cyanocyclopentyl)-4-methylpentanonitrile 19e (R = Me, Z = CN). The reaction of 4-methyl-3-penten-1-yl iodide with TBTH, in the presence of 15-fold excess of acrylonitrile afforded the title compound 19e in 65% yield. IR: 2985, 2890, 2250, 2240, 1480, 1460, 1400, 1380 cm^{-1} . $^1\text{H-NMR}$: 0.90 and 0.97 (ss from one isomer) and 1.05 and 1.10 (ss from other isomer) 6H (two methyl groups), 1.50-2.15 (m, 9H); 2.20-2.60 (t, 2H); 2.75-3.00 (m, 1H).

Ethyl 4-(2-ethoxycarbonylcyclopentyl)-4-methylpentanecarboxylate 19f (R = Me, Z = COOEt). When the reaction of 4-methyl-3-penten-1-yl iodide with TBTH was performed in the presence of 15-fold excess of ethyl acrylate, the title compound 19f was obtained in 75% yield. IR: 2970, 2880, 1740, 1380, 1180, 1160, 1050 cm^{-1} . $^1\text{H-NMR}$: 0.85 and 0.90 (ss, 6H); 1.25 (t, 6H); 1.40-2.00 (m, 9H); 2.05-2.90 (m, 3H), 3.90-4.25 (qq, 4H).

2-(2-Acetylcyclopentyl)-2-methyl-5-oxohexane 19g (R = Me, Z = COMe). 4-Methyl-3-penten-1-yl iodide was reduced by TBTH in the presence of 15-fold excess of methyl vinyl ketone affording the title compound 19g in 75% yield. IR: 2960, 2890, 1710, 1370, 1360, 1170 cm^{-1} . $^1\text{H-NMR}$ 0.65 and 0.70 (ss, 6H); 1.10-1.90 (m, 9H); 2.05 (s, 3H), 2.10 (s, 3H); 2.20-3.00 (m, 3H). Analysis: found: C, 74.75%; H, 10.80%; $\text{C}_{14}\text{H}_{24}\text{O}_2$ requires: C, 75.00, H, 10.71%.

4-(2-Formylcyclopentyl)-4-methylpentanal 19h (R = Me, Z = CHO). This cyclopentane derivative 19h was obtained in the reaction of 3-alkenyl iodide 18h with TBTH in the presence of ten-fold excess of acrolein (60% yield). IR: 2960, 2880, 2720, 1725, 1475, 1455, 1395, 1375 cm^{-1} . $^1\text{H-NMR}$: 0.85 (s, 6H); 1.20-2.10 (m, 9H); 2.20-2.70 (m, 3H); 9.75 (d, J = 5 Hz, 1H); 9.85 (t, J = 3 Hz, 1H).

4-(2-Cynocyclopentyl)-butironitrile 19i (R = H, Z = CN). By reaction of 3-butenyl bromide with TBTH in the presence of ten-fold excess of acrylonitrile, the title compound 19i was formed in 58% yield. IR: 2950, 2880, 2245, 2240, 1460, 1430 cm^{-1} . $^1\text{H-NMR}$: 0.90-2.70 (m, 13H); 2.85-3.25 (m, 1H).

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