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Reductive Cyclization of α-Cyclopropylketones with Alkynyl- and Aryl-Tethered Substituents

Maurizio Fagnoni[b,c], Philip Schmoldt[a)], Thorsten Kirschberg[b)], and Jochen Mattay[*a)]

a) Institut für Organische Chemie, Universität Kiel, Olshausenstr. 40, D – 24098 Kiel, Germany (Fax: +49-431-880-7410, E-mail: mattay@oc.uni-kiel.de)
b) Organisch-Chemisches-Institut, Universität Münster, Corrensstr. 40, D – 48149 Münster, Germany
c) Dipartimento di Chimica Organica , Università di Pavia,, Viale Taramelli 10, I – 27100 Pavia, Italy

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Abstract:

Photoinduced electron transfer (PET) reactions of α-cyclopropyl-substituted ketones and triethylamine (TEA) were used to initiate the cyclopropylcarbinyl-homoallyl rearrangement. The intramolecular cyclization reaction onto triple bonds was performed yielding bicyclic and spirocyclic compounds. Furthermore, in some preliminary studies it was shown that even intramolecular aromatic substitutions are feasible.

Keywords:
electron transfer; photochemistry; cleavage reactions; cyclization

1. Introduction

The area of synthetically useful photoinduced electron transfer (PET) reactions is continuously [1-11] increasing. We are presenting now a further application of the well-known PET reaction between photochemically excited ketones and triethylamine (TEA) as an electron source [10, 12, 13]. This reaction delivers a ketyl radical anion [10], which can also be formed by an electrochemical reduction [14], with samarium diiodide [15], or using dissolved metals like sodium or potassium in liquid ammonia [16]. Recently two reaction procedures have been introduced which make use of different PET reaction conditions [10]. The irradiation of the ketone in 20% TEA solution of ethanol [17] and the use of $LiClO_4$ as an additive to an acetonitrile solution of the ketone and TEA [18]. Both reaction conditions give better yields according to the authors but are mechanistically not yet fully understood. This article focuses on ketones substituted by an cyclopropyl moiety at the α carbon. For an example see Scheme 1 [12, 13].

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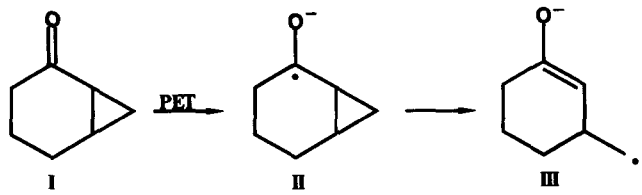


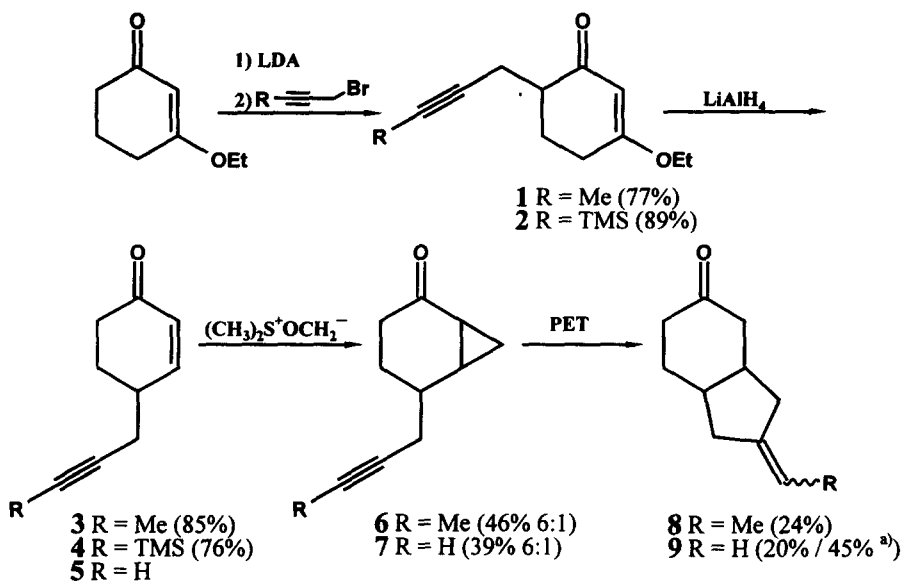
Scheme 1: Basic process of α-cyclopropyl substituted ketones upon one electron reduction

After one electron reduction of **I** a ketyl radical anion **II** is produced which undergoes the cyclopropylcarbinyl-homoallyl rearrangement to yield the intermediate **III**. Transformations which make use of this intermediate were of interest to us and tandem fragmentation cyclization reactions of various unsaturated substituted compounds have already been investigated [9, 12, 13]. The incorporation of the α-cyclopropyl-substituted ketone moiety into a bicyclic [n.1.0] system (n =3, 4) leads to the homolytic cleavage of the *exo*-cyclic bond due to the favorable overlap of the orbital containing the unpaired electron and the antibonding cyclopropyl orbital of the *exo*-cyclic C-C junction. **III** is the key intermediate which contains an enolate substructure and a remote radical center for further transformations. We are now describing a further extension of the already known cyclization reaction onto triple bonds present in the starting material leading to new bicyclic and spirocyclic compounds. By using aromatic side chains hexahydroanthracenones are accessible.

2. Intramolecular Cyclizations via Triple Bonds

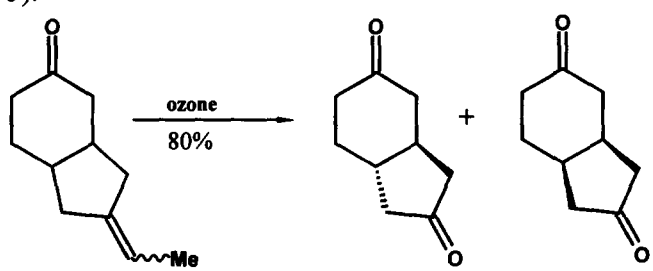
The synthesis of starting materials suitable for a cyclization reaction is depicted in Scheme 2. Alkylation of ethoxycyclohexenone with suitable alkynyl halides using LDA under kinetic conditions led to the α′alkylated products **1** and **2** which were reduced with $LiAlH_4$ to yield the 4-alkylated cyclohexenones **3** and **4**. The cyclopropanization following Corey's method led to the formation of the bicyclo[4.1.0]heptan-2-ones **6** and **7** in moderate yields as a mixture of two diastereomers with an excess of the *trans*-isomer. Analogeous observations were already made for allyl-substituted systems and the rel. configuration was proven by NOE experiments and analysis of the coupling constants of the protons 5-H, 6-H and 7-H [13]. The determination of the stereochemistry was important since it should not be affected by the following PET reaction. In order to reduce the numbers of possible stereoisomers arising from the PET reaction **4** was desilylated. Fortunately the proton at the terminal alkynyl group of compound **5** was tolerated in the following cyclopropanization reaction.

The PET reactions were performed in pyrex tubes at a wavelength of 300 nm using dry acetonitrile and an excess of 5 equivalents of TEA. The solutions were purged with argon before irradiation to assure the absence of oxygen. The PET reaction of compound **6** and **7** led to the expected cyclization products **8** and **9**.



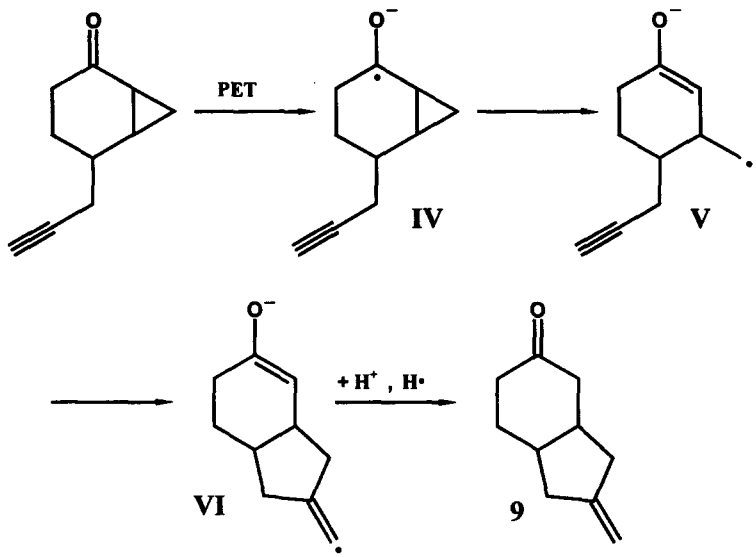
Scheme 2: Synthesis and reductive cyclization of compounds **6** and **7** ([a]) addition of 1 equiv. of $LiClO_4$, 254 nm)

In the case of irradiation of compound **6** four isomers were isolated as a mixture arising from the *cis* and *trans*-fused starting material and the two possible isomers resulting from the new *exo*-cyclic ethenyl group. Therefore an ozonolysis of the isomeric mixture of **8** was carried out yielding two isomeric diketones **10 a** and **10 b** in a ratio corresponding to that of the starting material **6** (Scheme 3).



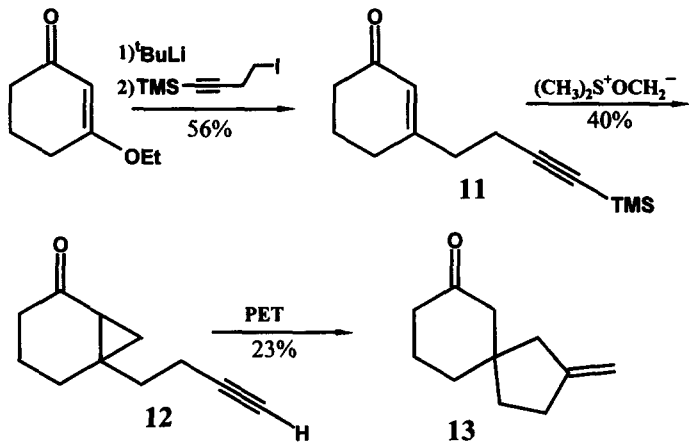
Scheme 3: Ozonolysis of compound **8**

A possible mechanistic interpretation for the formation of the products is given in the following Scheme 4. The one electron reduction of the bicyclic starting material initiated by the PET reaction yields the ketyl radical anion **IV** which undergoes the cyclopropylcarbinyl homoallyl radical rearrangement to the key intermediate **V**. The cyclization is achieved by the following radical attack onto the triple bond producing the intermediate **VI** which finally yields product **9** after hydrogen abstraction and protonation.



Scheme 4: Assumed mechanism of the PET reaction

By this procedure spirocyclic compounds should also be accessible starting from suitably substituted cyclopropyl ketones such as **12**. During the cyclopropanization of **11** the terminal alkynyl group was deprotected indicating again that a terminal alkyne group is tolerated by this kind of reaction.

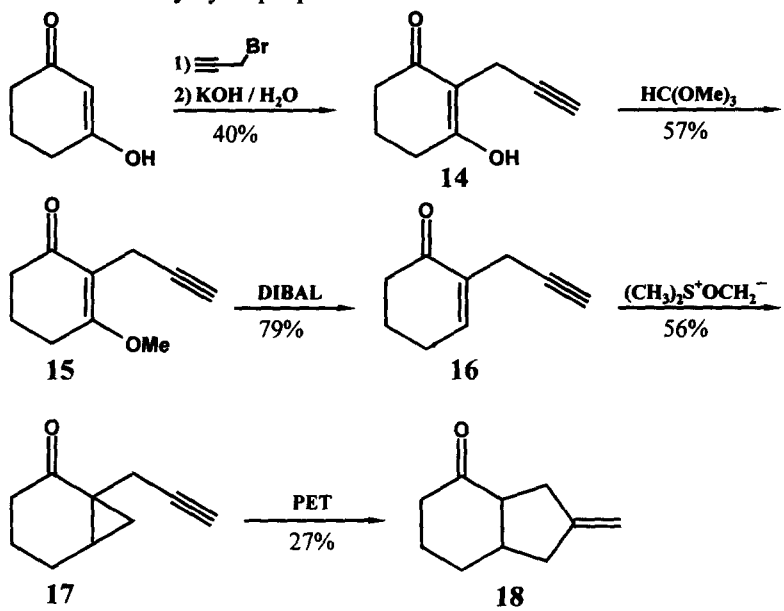


Scheme 5: Synthesis and reductive cyclization of **12**

The PET reaction of the bicyclic compound **12** yields the spirocyclic product **13** without any side products detectable by chromatographic analysis rather than by isolation.

Ring-annelated products of another kind can be synthesized via this PET method starting from compound **17**. The four step synthesis to produce the necessary starting material is outlined in Scheme 6. The alkylation of the 1,3-diketone under basic conditions introduced the

side chain into the 2-position followed by two steps providing the α,β-unsaturated enone which was converted to **17** by cyclopropanization.



Scheme 6: Synthesis and reductive cyclization of compound **17**

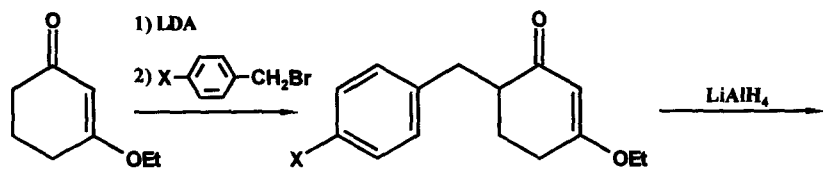
Again the PET reaction led to the formation of only one product **18** in moderate yields which can be rationalized according to the mechanism outlined above.

3. Intramolecular Aromatic Substitution Reactions

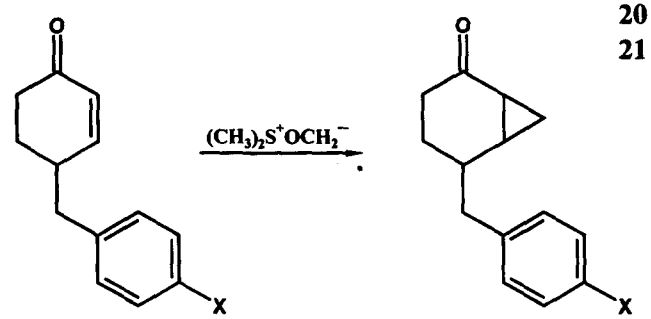
In order to expand the scope of the PET reaction bicyclic compounds bearing aromatic side-chains were synthesized as depicted in Scheme 7. The length of the side chain was chosen to allow for a *6-endo* or eventually *5-exo* cyclization reaction.

As in the synthesis of **6** and **7** the kinetic alkylation of ethoxycyclohexenone with substituted benzyl bromides using LDA yielded the α'-alkylated products **19-21**. Reduction with $LiAlH_4$ gave the enones **22-24** which were transformed to compounds **25-27** by cyclopropanization following Corey's method.

Just as for the alkenyl and alkynyl substituents the last reaction step mainly led to the formation of the *trans* isomer which was again proven by NOE experiments and the coupling pattern of 5-H, 6-H and 7-H.



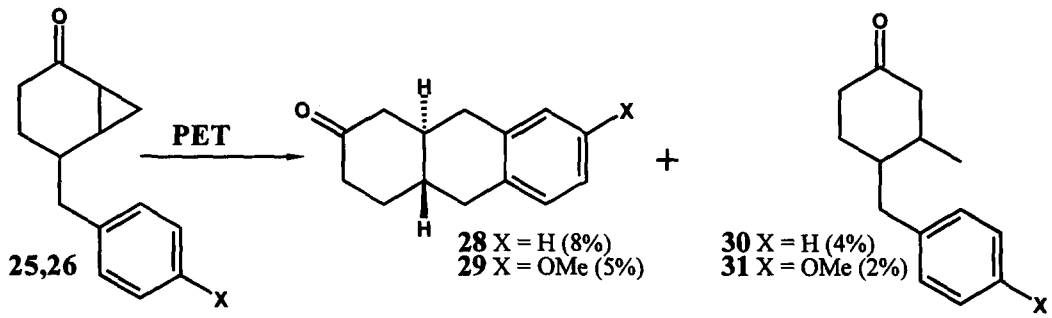
19 X = H (87%)
20 X = OMe (81%)
21 X = CN (75%)



22 X = H (90%)
23 X = OMe (90%)
24 X = CN (43%)

25 X = H (34%)
26 X = OMe (44%)
27 X = CN (30%)

Scheme 7: Synthesis of compounds **25-27**



28 X = H (8%)
29 X = OMe (5%)

30 X = H (4%)
31 X = OMe (2%)

Scheme 8: Products **28-31** resulting from the PET reaction

The PET reaction for these compounds yielded two different types of products in low yields along with approximately 20% of starting material. First the expected intramolecular cyclization products **28** (in addition to 5% of the corresponding 2-hydroxy-hexahydroanthracene – reduction product of **28**) and **29** and second the methyl substituted products **30** and **31**. With respect to the stereochemistry of the starting material compounds **28** and **29** were ascribed a *trans* junction of the two cyclohexane rings since there should be no alteration during the irradiation procedure. One reason for the small yields might result from a generally low reactivity of arenes in this type of radical substitution process. Another one might be due to an unfavourable substitution pattern of the arene. In case of compound **27** no product could be isolated which might be explained by a competing electron transfer reaction between the cyano substi-

tuted arene moiety and TEA thus preventing the reduction of the carbonyl group. Therefore our inital intention to increase the yield of the cyclization by activating the arene for the attack of the radical intermediate originating from the PET reaction was unsuccessful.

Although our studies on intramolecular aromatic substitutions remain preliminary and somewhat unsatisfactory the PET reactions of α-cyclopropyl substituted ketones provided with an alkenyl [12,13] or an alkynyl side chain and TEA is a versatile tool for the construction of bi-, tricyclic and spirocyclic compounds. As we already have shown earlier [13] in our hands the PET method yields comparable results like the use of SmI_2 [15]. Moreover, the utilization of salt effects e.g. by addition of $LiClO_4$ results in a nearly doubling of the yield.

4. Experimental section

Diethyl ether and THF were dried by refluxing over $LiAlH_4$ for 5 h, then distilled and stored under argon. DMSO and DMF were stored under argon and over molecular sieves (4A, 8-12 mesh) and used without further purification. Toluene and pentane were freshly distilled and stored over molecular sieves (4A, 8.12 mesh) and acetonitrile was distilled from P_2O_5 and stored under argon. NEt_3 was stored over NaOH and passed over alumina just before use. DMSO·MeI was crystallized from water and dried in vacuo for 1 day. Reactions involving dry solvents were carried out using dry glassware.

Synthesis of 5-alkyl-bicyclo[4.1.0]heptan-2-one: general procedure

Synthesis of 3-ethoxy-6-alkyl-cyclohex-2en-1-one: general procedure A

The compounds were prepared following a general procedure described by Stork[19]. Diisopropylamine (7.8 mL, 55 mmol) in THF (100 mL) was placed in a flask under argon atmosphere and cooled to -20 °C with an ice/salt bath and then *n*-BuLi (35 mL, solution 1.6 M in hexane) was added under stirring. The solution of LDA thus formed was cooled to -78 °C with an acetone/dry ice bath and 3-ethoxy-cyclohex-2-en-1-one (7.0 mL, 50 mmol) in 12.5 mL THF was added over a period of 1 h. After 45 min the solution of the alkyl halide (55 mmol in 10 mL of THF) was added over 15 min. The solution was allowed to remain at -78 °C for 2.5 h and after the removal of the bath another 1.5 h in order to reach room temperature. 5 mL water were added to the mixture, the resulting two phases were separated and the aqueous layer (with an additional amount of water) was extracted two times with diethyl ether. The combined organic phases were washed with brine and dried over $MgSO_4$.

Synthesis of 4-alkyl-cyclohex-2-en-1-one: general procedure B

The compounds were prepared analogous to the procedure by Stork[19]. $LiAlH_4$ (558 mg) was added to a solution of the former compound (39 mmol) in diethyl ether (150 mL) in small portions under argon and the resulting mixture was heated under reflux for 2 h. The working up procedure consisted of adding water, followed by HCl (2N) under stirring and then allowing vigorous stirring for 30 min. The water phase was extracted two times with diethyl ether, the combined ether phases were washed with $NaHCO_3$ solution and then dried over $MgSO_4$.

Synthesis of 5-alkyl-bicyclo[4.1.0]heptan-2-one: general procedure C

The compounds were prepared analogous to Corey's method[20]. NaH (0.96 g, 50-60% dispersion in mineral oil) was washed three times with pentane in a three neck flask under argon atmosphere. After the remaining solvent was removed in vacuo the argon atmosphere was restored. DMSO·MeI (3.73 g) was then added followed by dropwise addition of DMSO (50 mL) under stirring. After the evolution of gas had ceased the solution of the enone (16.1 mmol in 3 mL DMSO) was added during 20 min and the mixture was stirred for 5 h under argon. The working up procedure consisted of pouring the mixture into ice/water (100 mL) and extracting the water phase 4 times with diethyl ether. The combined ether phases were washed with brine and dried over $MgSO_4$.

3-Ethoxy-6-(butyn-2-yl)-cyclohex-2-en-1-one (1). This compound was prepared following the general method A starting from 4.8 mL of diisopropylamine, 21.5 mL of *n*-BuLi, 4.3 mL of 3-ethoxy-cyclohex-2-en-1-one and 4.5 g (33.8 mmol) of 1-bromo-2-butyne [21]. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 8:2) yielding a white solid: 5 g (77%). A small amount was crystallized from cyclohexane/pentane m.p. 77-78°C. - ^{1}H NMR ($CDCl_3$) δ 1.35 (t, 3H, J=7Hz), 1.77 (t, 3H, J=2.6Hz), 1.8 (m, 1H), 2.3 (m, 3H), 2.45 (m, 2H), 2.7 (dq, 1H, J=2.6Hz, J=15.8Hz), 3.9 (dq, 2H, J=2.6Hz, J=7Hz), 5.35 (s, 1H). ^{13}C NMR (C_6D_6) δ 3.73 (CH_3), 14.27 (CH_3), 20.34 (CH_2), 26.98 (CH_2), 29.12 (CH_2), 45.44 (CH), 64.16 (CH_2), 77.13 (C triple bond), 78.11 (C triple bond), 103.03 (CH), 176.22 (CH), 197.43 (CO). IR 2947, 1660, 1632, 1253, 1199 cm^{-1}. MS m/z = 193 M^++1(100). Anal. Calcd. for $C_{12}H_{16}O_2$ (M.W.= 192): C, 74.97; H, 8.39; found: C, 74.77;H, 8.42.

4-(Butyn-2-yl)-cyclohex-2-en-1-one (3). This compound was prepared following the general method B starting from 4.6 g of **1** (24 mmol) and 343 mg of $LiAlH_4$. The crude product was purified by column (cyclohexane/ethyl acetate 8:2) yielding an oil: 3 g (85%). - ^{1}H NMR ($CDCl_3$) δ 1.80 (t, 3H, J=2.6Hz), 1.85 (m, 1H), 2.15 (m, 1H), 2.30 (m, 2H), 2.40 (m, 1H), 2.50 (dt, 1H, J=4.5Hz, J=16.7Hz), 2.60 (m, 1H), 6.00 (br d, 1H, J=10Hz), 6.95 (br d, 1H, J=10Hz). ^{13}C NMR ($CDCl_3$) δ 3.42 (CH_3), 24.44 (CH_2), 28.52 (CH_2), 36.14 (CH), 36.88 (CH_2), 76.00 (C triple bond), 77.92 (C triple bond), 129.68 (CH), 153.30 (CH), 199.40 (CO). IR 2927, 1692, 1394 cm^{-1}. MS m/z = 148 M^+(9), 120(65), 91(100).

5-(Butyn-2-yl)-bicyclo[4.1.0]heptan-2-one (6) (trans isomer). This compound was prepared following the general method C starting from 3 g of **3** (20.3 mmol), 1.21 g of NaH and 4.70 g of DMSO·MeI. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 1.5 g (46%) which is a mixture *cis/trans* 1:6 (calculated from ^{13}C NMR). - ^{1}H NMR (C_6D_6) δ 0.55 (m, 2H), 1.1-1.4 (m, 3H), 1.5-1.6 (m, 3H), 1.55 (t, 1H, J=2.5Hz), 1.8 (m, 2H), 1.9-2.1 (m, 3H); ^{13}C NMR (C_6D_6) δ 4.05 (CH_3), 12.27 (CH_2), 23.65 (CH), 24.56 (CH_2), 25.27 (CH_2), 26.16 (CH), 33.00 (CH), 33.56 (CH_2), 77.85 (C triple bond), 78.29 (C triple bond), 206.40 (CO). IR 2927, 1699, 1359 cm^{-1}. MS m/z = 162 M^+(39), 39(100). Anal. Calcd. for $C_{11}H_{14}O$ (M.W.=162): C, 81.44; H, 8.70; found: C, 80.99; H, 8.73.

3-Ethoxy-6-(trimethylsilyl-2-propynyl)-cyclohex-2-en-1-one (2). This compound was prepared following the general method A starting from 4.9 mL of diisopropylamine, 22 mL *n*-BuLi, 4.1 mL of 3-ethoxy-cyclohex-2-en-1-one and 5 mL (35.3 mmol) of 3-(trimethylsilyl)-propargyl bromide. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 8:2) yielding a white solid: 7.7 g (90%). A small amount was crystallized from pentane m.p. 78-79°C. - ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9H), 1.2 (t, 3H, J=7Hz), 1.65 (m, 1H), 2.2 (m, 3H), 2.35 (m, 2H), 2.75 (dd, 1H, J=3.4Hz, J=16.4Hz), 3.75 (dq, 2H, J=3Hz, J=7Hz), 5.2 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 0.00 ($3CH_3$), 14.01 (CH_3), 20.48 (CH_2), 26.07 (CH_2), 28.57 (CH_2), 44.21 (CH), 64.19 (CH_2), 85.92 (C triple bond), 102.00 (CH), 105.10 (C triple bond), 177.21, 198.59 (CO). IR 2963, 2182, 1692, 1614, 1252, 847 cm^{-1}. MS m/z = 250 M^+(24), 222(100). Anal. Calcd. for $C_{14}H_{22}O_2Si$ (M.W.=250): C, 67.15; H, 8.86; found: C, 67.08; H, 8.82.

4-(Trimethylsilyl-2-propynyl)-cyclohex-2-en-1-one (4). This compound was prepared following the general method B starting from 7.7 g of **2** (30.8 mmol) and 440 mg of $LiAlH_4$. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 4.8 g (76%). - ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9H), 1.65 (m, 1H), 2.00 (m, 1H), 2.15-2.30 (m, 3H), 2.40 (dt, 1H, J=4.5Hz, J=16.7Hz) 2.50 (m, 1H), 5.85 (br d, 1H, J=10Hz), 6.75 (br d, 1H, J=10Hz). ^{13}C NMR ($CDCl_3$) δ 0.00 ($3CH_3$), 25.38 (CH_2), 28.47 (CH_2), 35.76 (CH), 36.77 (CH_2), 87.18 (C triple bond), 103.66 (C triple bond), 129.77 (CH), 152.64 (CH), 199.16 (CO). IR 2960, 2183, 1692, 1694, 847 cm^{-1}. MS m/z = 205 M^+-1(3), 191(100) Anal. Calcd. for $C_{12}H_{18}OSi$ (M.W.=206): C, 69.84; H, 8.79; found: C, 69.53; H, 9.07.

4-(2-Propynyl)-cyclohex-2-en-1-one (5). This compound was prepared following the procedure of Gleiter[22] for the desilylation of terminal alkynes. A solution of 2.4 g (11.7 mmol) of **4** in 8 mL of THF/DMF (4:6) was treated with 1.8 g of $KF{\cdot}H_2O$ for 48 h at room temperature. After addition of 5 mL of water, the mixture was extracted with diethyl ether. The organic phase was washed with brine and dried over $MgSO_4$. After the removal of the solvent the crude product was purified by column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 920 mg (59%). - ^{1}H NMR ($CDCl_3$) δ 1.80 (m, 1H), 2.00 (t, 1H, J=2.6Hz), 2.15 (m, 1H), 2.30 (m, 3H), 2.45(dt, 1H, J=4.7Hz), 2.60 (m, 1H), 5.95 (br d, 1H, J=10Hz), 6.85 (br d,1H, J=10Hz). ^{13}C NMR ($CDCl_3$) δ 23.99 (CH_2), 28.37 (CH_2), 35.52 (CH), 36.7 (CH_2), 70.6 (C triple bond), 81.1 (C triple bond), 129.9 (CH), 152.4 (CH), 198.99 (CO). IR 3297, 2956, 2125, 1685 cm^{-1}. MS m/z = 134 M^+(9), 91(84), 78(100).

5-(2-Propynyl)bicyclo[4.1.0]heptan-2-one (7). This compound was prepared following the general method C starting from 920 mg of **5** (6.9 mmol), 0.41 g of NaH and 1.6 g of DMSO·MeI. In this case the enone was added at 18 °C and the mixture became coloured (green-blue) but the colour disappeared during the working up procedure. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 400 mg (40%) which is a mixture *cis/trans* 1:6 (calculated from ^{13}C NMR). - ^{1}H NMR ($CDCl_3$) δ 1.1 (m, 2H), 1.65 (m, 4H), 1.90 (t, 1H, J=2.6Hz), 2.05 (m, 2H), 2.20 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 12.22 (CH_2), 23.25 (CH), 23.25 (CH_2), 23.85 (CH_2), 25.37 (CH), 31.33 (CH), 32.54

(CH_2), 69.98 (C triple bond), 82.22 (C triple bond), 208.54 (CO). IR 3297, 3020, 2920, 2118, 1706, 1359 cm^{-1}. MS m/z = 149 M^++1(36), 91(70), 39(100). Anal. Calcd. for $C_{10}H_{12}O$ (M.W.=148): C, 81.04; H, 81.16; found: C, 80.69; H, 8.03.

3-(4-Trimethylsilyl-3-butynyl)-cyclohex-2-en-1-one (11). This compound was prepared following the procedure of Motherwell [23] for the synthesis of a similar enone. 4.7 g (18.8 mmol) of 4-iodo-1-trimethylsilylbut-1-yne [24] were dissolved in pentane and cooled to -78 °C under argon. 12 mL (solution 1.7M in pentane) of *t*-butyllithium were added dropwise over 5 min under stirring. After 1 h of stirring the mixture was transferred to a vessel containing 3.76 g 3-ethoxycyclohex-2-en-1-one in THF (120 mL) via a lagged cannula at -78 °C under argon. After further stirring for 1 h the mixture was allowed to warm to room temperature. Distilled water (5 mL) was added followed by removal of solvents in vacuo. 2M HCl (100 mL) and THF (100 mL) were added to the residue and the homogeneous mixture was then stirred for 2 h at room temperature. The mixture was then neutralized with aqueous $NaHCO_3$ and extracted with diethyl ether (3x80 mL). The combined organic phases were dried over $MgSO_4$ before removal of the solvents in vacuo. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 2.3 g (56%). - ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H), 1.9 (m, 2H), 2.25 (m, 4H), 2.3 (s, 4H), 5.82 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 0.00 ($3CH_3$), 18.07 (CH_2), 22.62 (CH_2), 29.59 (CH_2), 36.66 (CH_2), 37.31 (CH_2), 86.13 (C triple bond), 105.13 (C triple bond), 126.44 (CH), 163.72, 199.59 (CO). IR 2960, 2182, 1680, 1254, 854 cm^{-1}. MS m/z = 219 M^+-1(5), 118(97), 73(100). Anal. Calcd. for $C_{13}H_{20}OSi$ (M.W.=220): Observed M^+-1=219.1203; required 219.1205.

1-(3-Butynyl)bicyclo[4.1.0]heptan-5-one (12). This compound was prepared following the general method C starting from 2.3 g (10.4 mmol) of **10**, 0.62 g NaH and 2.42 g of DMSO·MeI. In this case cyclopropanization and desilylation took place in only one step. After the addition of the enone the mixture became coloured (green-blue) but the colour disappeared during the working-up procedure. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 680 mg (40%). - ^1H NMR ($CDCl_3$) δ 1.0 (dd, 1H, J=5Hz, J=10Hz), 1.4 (dd, 1H, J=5Hz, J=5Hz), 1.56 (m, 2H), 1.61 (m, 1H), 1.65 (t, 1H, J=7Hz), 1.68-1.76 (m, 2H), 1.92 (t, 1H, J=2.6Hz), 1.94-2.2 (m, 2H), 2.2-2.3 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 17.43 (CH_2), 18.47 (CH_2), 19.92 (CH_2), 26.86 (CH_2), 29.05, 35.08 (CH), 37.87 (CH_2), 39.36 (CH_2), 70.80 (C triple bond), 85.32 (C triple bond), 210.34 (CO). IR 3291, 2947, 2121, 1694, 1254 cm^{-1}. MS m/z = 162 M^+(9), 91(100). Anal. Calcd. for $C_{11}H_{14}O$ (M.W.=162): Observed M^+162.1041; required 162.1044.

2-(2-Propynyl)-1,3-cyclohexandione (14). This compound was prepared following a procedure described by Büchi [25] for the synthesis of an analogous 2-alkyl-1,3-cyclohexadione. 20.2 mL (269.1 mmol) propargyl bromide were added to an ice cold solution of 30 g (267.5 mmol) 1,3-cyclohexandione in 18.66 g KOH and 60 mL water. The reaction mixture was stirred for 15 h at room temperature and then 3 h at 40 °C. The mixture was poured into 4M NaOH (170 mL) and washed twice with diethyl ether for removal of the neutral compounds. The aqueous solution was acidified with cold HCl solution (140 g of concentrated HCl in 140 g of crushed ice).

A precipitate was obtained after filtration, washing with water and drying in vacuo and was further purified by column chromatography (cyclohexane/ethyl acetate 3:7) to give one light-yellow solid 13.4 g (40%). A small amount was crystallized from cyclohexane/ethyl acetate m.p. 136-138 °C. - ^{1}H NMR (CD_3OD) δ 1.88 (quint, 2H, J=6Hz), 1.92 (t, 1H, J=2.6Hz), 2.35 (t, 4H, J=6Hz), 3.00 (d, 2H, J=2.6Hz), 4.75(s, 1H). IR 3310, 2936, 2115, 1712, 1580, 1390 cm^{-1}. MS m/z = 150 M^+(38), 94(100). Anal. Calcd. for $C_9H_{10}O_2$ (M.W.=150): C, 71.98; H, 6.71; found: C, 71.83; H, 6.81.

3-Methoxy-2-(2-propynyl)-cyclohex-2-en-1-one (15). This compound was prepared following Motherwell's procedure [22] for the synthesis of the analogous cyclohexenone. 12.8 g (85.3 mmol) of the dione **14** were dissolved in MeOH (600 mL) and 83 mL trimethyl orthoformate were added followed by 5.2 mL conc. H_2SO_4. The solution was stirred at room temperature for 6 h. The solution was then neutralized with a saturated solution of $NaHCO_3$ and most of the MeOH was removed by distillation in vacuo. The mixture was then extracted with $CHCl_3$ (3x350 mL) and the combined organic phases were dried over $MgSO_4$. The resulting crude product was purified by column chromatography (cyclohexane/ethyl acetate 3:7) yielding a yellow solid 8 g (57%). A small amount was crystallized from cyclohexane/ethyl acetate m.p.97-99 °C. - ^{1}H NMR ($CDCl_3$) δ 1.8 (t, 1H, J=2.6Hz), 2.0 (quint, 2H, J=6Hz), 2.4 (t, 2H, J=6Hz), 2.6 (t, 2H, J=6Hz), 3.20 (d, 2H, J=2.6Hz), 3.9 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 11.57 (CH_2), 20.61 (CH_2), 24.93 (CH_2), 36.08 (CH_2), 55.56 (CH_3), 65.87 (C triple bond), 83.29 (C triple bond), 114.76, 173.03, 196.62 (CO). IR 3237, 2959, 1646, 1382, 1243 cm^{-1}. MS m/z = 164 M^+(8), 149(100) Anal. Calcd. for $C_{10}H_{12}O_2$ (M.W.=164): C, 73.15; H, 7.37; found: C, 73.02; H, 7.45.

2-(2-Propynyl)-cyclohex-2-en-1-one (16). This compound was prepared analogous to Motherwell's procedure [22] for the synthesis of a similar cyclohexenone. Ketone **15** (4.5 g, 27.4 mmol) was dissolved in 90 mL of toluene and cooled to 0 °C under argon. DIBAL (27.55 mL of a 1.5M solution in toluene) was added dropwise over 15 min. After stirring at 0 °C for 2h, water (25 mL) was added dropwise followed by 2M HCl (15 mL) and the mixture stirred vigorously for 30 min. The aqueous phase was then extracted with diethyl ether (2x25 mL) and the combined organic extracts were washed with a saturated solution of $NaHCO_3$ and then dried over $MgSO_4$. The resulting crude product was purified by column chromatography (cyclohexane/ethyl acetate 7:3) yielding an oil 2.9 g (79%). - ^{1}H NMR ($CDCl_3$) δ 2.0 (quint, 2H, J=6Hz), 2.18 (t, 1H, J=2.6Hz), 2.45 (m, 4H), 3.15 (m, 2H), 3.9 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 19.02 (CH_2), 22.98 (CH_2), 25.98 (CH_2), 38.20 (CH_2), 71.73 (C triple bond), 80.90 (C triple bond), 134.05, 146.27 (CH), 198.07 (CO). IR 3290, 2956, 1678, 1387 cm^{-1}. MS m/z = 133 M^+-1(100).

1-(2-Propynyl)bicyclo[4.1.0]heptan-2-one (17). This compound was prepared following the general method C starting from 2.6 g (19.4 mmol) of **16**, 1.16 g of NaH and 4.49 g of DMSO·MeI. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 9:1) yielding an oil: 1.6 g (56%). - ^{1}H NMR ($CDCl_3$) δ 1.2 (dd, 1H, J=5Hz, J=8Hz),

1.35 (dd, 1H, J=5Hz, J=5Hz), 1.7 (m, 2H), 1.9 (m, 4H), 2.1 (m, 1H), 2.35 (dt, 1H, J=5 Hz, J=18Hz), 2.6 (dd, 1H, J=2.6Hz, J=18Hz), 2.8 (dd, 1H, J=2.6Hz, J=18Hz). ^{13}C NMR ($CDCl_3$) δ 15.40 (CH_2), 19.11 (CH_2), 21.53 (CH_2), 21.63 (CH_2), 23.12 (CH), 31.47, 36.73 (CH_2), 69.61 (C triple bond), 80.80 (C triple bond), 208.60 (CO). IR 3297, 3013, 2942, 2125, 1692, 1365 cm^{-1}. MS m/z = 149 M^++1(41), 105(62), 91(100), 39(89).

3 Ethoxy-6-benzyl-cyclohex-2-en-1-one (19). This compound was prepared following the general procedure A starting from 7.8 mL (55 mmol) of diisopropylamine, 35 mL of *n*-BuLi, 7.0 mL of 3-ethoxy-cyclohex-2-en-1-one and 6.5 mL (54.7 mmol) of benzyl bromide. The crude product was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 10.2 g (89%). - ^1H NMR ($CDCl_3$) δ 1.35 (t, 3H, J=7Hz), 1.6 (m, 1H), 1.9 (m, 1H), 2.36 (m, 2H), 2.44 (m, 1H), 2.51 (dd, 1H, J=10.1Hz, J=13.5Hz), 3.37 (dd, 1H, J=3.1Hz, J=12.9Hz), 3.9 (dq, 2H, J=1.7Hz, J=7.1Hz), 5.4 (s, 1H), 7.2 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 14.14 (CH_3), 25.58 (CH_2), 28.24 (CH_2), 35.69 (CH_2), 47.08 (CH), 64.26 (CH_2), 102.24 (CH), 126.06 (CH), 128.35 (CH), 129.20 (CH), 140.20, 177.01, 200.33 (CO). IR 2935, 1663, 1614, 1195, 748, 705 cm^{-1}. MS m/z = 230 M^+(78), 139(80), 111(100) 91(64).

4-Benzyl-cyclohex-2-en-1-one (22). This compound was prepared following the general method B starting from 9.0 g (39 mmol) of **18** and 558 mg of $LiAlH_4$. The crude product was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 6.5 g (90%). - ^1H NMR ($CDCl_3$) δ 1.7 (m, 1H), 2.0 (m, 1H), 2.3 (m, 1H), 2.45 (dt, 1H, J=5Hz, J=16Hz), 2.7 (m, 3H), 5.95 (br d, 1H, J=11Hz), 7.2 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 28.57 (CH_2), 36.72 (CH_2), 37.91 (CH), 41.29 (CH_2), 126.47 (CH), 128.52 (CH), 128.96 (CH), 129.13 (CH), 138.9, 153.6 (CH), 199.2 (CO). IR 3034, 2928, 1692, 1458, 741, 705 cm^{-1}. MS m/z = 186 M^+(10), 91(100). Anal. Calcd. for $C_{13}H_{14}O$ (M.W.=186): Observed M^+=186.1046; required 186.1044.

5-Benzyl-bicyclo[4.1.0]heptan-2-one (25) (trans isomer). This compound was prepared following the general method C starting from 3.0 g (16.1 mmol) of **21**, 0.96 g of NaH and 3.73 g of DMSO·MeI. The crude product was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 1.1 g (34%). The reaction's major product was the *trans* isomer and its structure could be confirmed by NOE experiments studying the interaction of H-5, H-7 and H-7'. - ^1H NMR ($CDCl_3$) δ 1.15 (m, 1H), 1.25 (m, 1H), 1.6 (m, 2H), 1.8 (m, 2H), 2.2 (m, 2H), 2.4 (m, 1H), 2.73 (dd, 2H, J=8Hz, J=14Hz), 7.25 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 12.30 (CH_2), 23.02 (CH_2), 23.82 (CH), 25.64 (CH), 32.76 (CH_2), 33.46 (CH), 40.77 (CH_2), 126.23 (CH), 128.49 (CH), 128.94 (CH), 140.05, 209.30 (CO). IR 3027, 2935, 1706, 1359, 705 cm^{-1}. MS m/z = 200 M^+(3), 91(100). Anal. Calcd. for $C_{14}H_{16}O$ (M.W.=200): Observed M^+=200.1201; required 200.1201.

3-Ethoxy-6-(p-methoxybenzyl)-cyclohex-2-en-1-one (20). This compound was prepared following the general procedure A starting from 5.4 mL of diisopropylamine, 24 mL of *n*-BuLi, 4.8 mL of 3-ethoxy-cyclohex-2-en-1-one and 7.6 g (37.8 mmol) of 4-methoxybenzyl bromide [26]. The crude product was purified using column chromatography (cyclohexane/ethyl acetate

7:3) yielding a white solid: 7.2 g (81%). A small amount was crystallized from cyclohexane/pentane m-p. 66-67 °C. - ^{1}H NMR ($CDCl_3$) δ 1.35 (t, 3H, J=7Hz), 1.6 (M, 1H), 1.9 (m, 1H). 2.35 (m, 2H), 2.42 (m, 1H), 2.5 (dd, 1H, J=10Hz, J=13.3Hz), 3.3 (dd, 1H, J=3.3Hz, J=13.3Hz), 3.8 (s, 3H), 3.9 (q, 2H, J=7Hz), 5.3 (s, 1H), 6.8 (d, 2H, J=8.5Hz), 7.1 (d, 2H, J=8.5Hz). ^{13}C NMR ($CDCl_3$) δ 14.16 (CH_3), 25.52 (CH_2), 28.22 (CH), 34.80 (CH_2), 47.24 (CH), 55.26 (CH_3), 64.26 (CH_2), 102.30 (CH), 113.85 (CH), 130.14 (CH), 132.13, 158.05, 177.04, 200.57 (CO). IR 2935, 1664, 1628, 1259, 1209 cm^{-1}. MS m/z = 260 M$^+$(20), 121, (100). Anal. Calcd. for $C_{16}H_{20}O_3$ (M.W.=260): C, 73.82; H, 7.74; found; C, 73.79; H, 7.90

4-(p-Methoxybenzyl)-cyclohex-2-en-1-one (23). This compound was prepared following the general method B starting from 7.2 g (33 mmol) of **20** and 400 mg of $LiAlH_4$. The crude product was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 5.4 g (90%). - ^{1}H NMR ($CDCl_3$) δ 1.7 (m, 1H), 2.05 (m, 1H), 2.3 (m, 1H), 2.5 (dt, 1H, J=4.8Hz, J=16.6Hz), 2.7 (m,3H), 3.8 (s, 3H), 6.0 (dd, 1H, J=1.2Hz, J=10.2Hz), 6.8 (br d, 1H, J=10.2Hz), 6.85 (d, 2H, J=8.5Hz), 7.1 (d, 2H, J=8.5Hz). ^{13}C NMR ($CDCl_3$) δ 28.60 (CH_2), 36.80 (CH_2), 38.17 (CH), 40.04 (CH_2), 55.27 (CH_3), 114.01 (CH), 129.25 (CH), 129.97 (CH), 130.96, 153.86 (CH), 158.33, 199.60 (CO). IR 2947, 1687, 1618, 1253, 1040 cm^{-1}. MS m/z = 216 M$^+$(1), 121(100). Anal. Calcd. for $C_{14}H_{16}O_2$ (M.W.=216): C, 77.75; H, 7.46; found: C, 77.53; H, 7.62.

5-(p-Methoxybenzyl)-bicyclo[4.1.0]heptan-2-one (26). This compound was prepared following the general method C starting from 3.2 g (14 mmol) of **23**, 0.88 g of NaH and 3.43 g of DMSO·MeI. The crude product was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding an oil: 1.5 g (44%). The major product was the *trans* isomer and its structure confirmed by NOE experiments studying the interaction of H-5, H-7 and H-7′. - ^{1}H NMR ($CDCl_3$) δ 1.15 (m, 1H), 1.25 (m, 1H), 1.6 (m, 1H), 1.8 (m, 2H), 2.2 (m, 2H), 2.35 (m, 1H), 2.7 (dd, 2H, J=7.6, J=13.6 Hz), 3.8 (s, 3H), 6.85 (d, 2H, J=8.6 Hz), 7.1 (d, 2H, J=8.6 Hz). ^{13}C NMR ($CDCl_3$) δ 12.3 (CH_2), 22.8 (CH_2), 25.6 (CH_2), 32.7 (CH_2), 33.5 (CH), 39.8 (CH_2), 55.2 (CH_3), 113.8 (CH), 129.8 (CH), 132.0, 158.0, 209.6 (CO). IR 3016, 2933, 1701, 1253 cm^{-1}. MS m/z = 230 M$^+$(9), 121 (100). Anal. Calcd. for $C_{15}H_{18}O_2$ (M.W.=230): Observed M$^+$=230.1311; required 230.1307.

3-Ethoxy-6-(p-cyanobenzyl)-cyclohex-2-en-1-one (21). This compound was prepared following the general procedure A starting from 3.61 mL of diisopropylamine, 16.2 mL of *n*-BuLi, 3.0 mL of 3-ethoxy-cyclohex-2-en-1-one and 5.0 g (25.5 mmol) of 4-cyanobenzyl bromide. The crude product was purified using column chromatography (cyclohexane/ethyl acetate 6:4) yielding a white solid: 4.84 g (75%). A small amount was crystallized from cyclohexane m-p. 96-97 °C. - ^{1}H NMR ($CDCl_3$) δ 1.35 (t, 3H, J=7Hz), 1.6 (m, 1H), 1.9 (m, 1H), 2.4 (m, 2H), 2.48 (m, 1H), 2.66 (dd, 1H, J=9Hz, J=13.8Hz), 3.4 (dd, 1H, J=4.5Hz, J=13.8Hz), 3.9 (dq, 2H, J=2.1Hz, J=7Hz), 5.4 (s, 1H), 7.3 (d, 2H, J=8.3Hz), 7.58 (d, 2H, J=8.3Hz). ^{13}C NMR ($CDCl_3$) δ 14.13 (CH_3), 25.98 (CH_2), 28.54 (CH_2), 35.96 (CH_2), 46.70 (CH), 64.46 (CH_2), 102.23 (CH), 110.09, 118,99 (CN), 130.10 (CH), 132.18 (CH), 146.15, 177.15, 199.25 (CO). IR 2929, 2225,

1654, 1617 cm^{-1}. MS m/z = 255 M^+(90), 139(84), 111(100). Anal. Calcd. for $C_{16}H_{17}NO_2$ (M.W.=255): C, 75.27;H, 6.71; N=5.49; found: C, 75.41; H, 6.64; N, 5.76.

*4-(p-Cyanobenzyl)-cyclohex-2-en-1-one (**24**).* This compound was prepared following the general procedure of Gemal [27] for the reduction of enones. 12.8 g of $CeCl_3 \cdot H_2O$ and 8.67 g (34 mmol) of **21** were dissolved in 90 mL of MeOH. 1.32 g $NaBH_4$ were added in one portion under stirring. A vigorous gas evolution occurred and the temperature rose to about 35-40 °C. Stirring was continued for 20 min before the pH was adjusted to neutrality with diluted aqueous HCl, the mixture was then extracted two times with ether and the ether phases were dried over $MgSO_4$. The crude product was purified using column chromatography (cyclohexane/ethyl acetate 6:4) yielding an oil: 3.1 g (43%). - ^{1}H NMR ($CDCl_3$) δ 1.75 (m, 1H), 2.05 (m, 1H), 2.35 (m, 1H), 2.5 (dt, 1H, J=5Hz, J=17Hz), 2.85 (m, 3H), 6.0 (dd, 1H, J=1.4Hz, J=10Hz), 6.8 (br d, 1H, J=10Hz), 7.35 (d, 2H, J=8Hz), 7.65 (d, 2H, J=8Hz). ^{13}C NMR ($CDCl_3$) δ 28.56 (CH_2), 36.62 (CH_2), 37.53 (CH_2), 40.97 (CH_2), 110.68, 118.71 (CN), 129.85 (CH arom), 129.85 (CH vinyl), 132.44 (CH), 144.58, 152.37 (CH), 198.94 (CO). IR 2951, 2233, 1690, 1610, 862 cm^{-1}. MS m/z = 211 M^+(31), 116(100). Anal. calcd. for $C_{14}H_{13}NO$ (M.W.=211): Observed M^+=211.0975; required 211.0997.

*5-(p-Cyanobenzyl)-bicyclo[4.1.0]heptan-2-one (**27**).* This compound was prepared following the general method C starting from 3.1 g (14.7 mmol) of **24**, 0.88 g of NaH and 3.40 g of DMSO·MeI. During the reaction the formation of polymer occurred probably due to the interaction between the cyano group and the ylide formed. This led to the synthesis of a large amount of the undesired isomer yielding a (1:3) *cis/trans* mixture (calculated from ^{13}C). The crude product was purified using column chromatography (cyclohexane/ethyl acetate 6:4) yielding an oil: 1.0 g (30%). - ^{1}H NMR ($CDCl_3$) δ 1.2 (m, 1H), 1.3 (m, 1H), 1.55 (m, 2H), 1.8 (m, 2H), 2.2 (m, 2H), 2.4 (m, 1H), 2.75 (dd, 1H, J=13.5Hz), 2.85 (dd, 1H, J=7.6Hz, J=13.5Hz), 7.3 (d, 2H, J=8.5Hz), 7.6 (d, 2H, J=8.5Hz). ^{13}C NMR ($CDCl_3$) δ 12.29 (CH_2), 23.15 (CH_2), 23.61 (CH), 25.57 (CH), 32.65 (CH_2), 33.32 (CH_2), 40.90 (CH_2), 110.35, 118.85 (CN), 129.90 (CH), 132.37 (CH), 145.70, 208.58 (CO). IR 2937, 2233, 1690, 1610 cm^{-1}. MS m/z = 225 M^+(13), 109(78), 81(100). Anal. Calcd. for $C_{15}H_{15}NO$ (M.W.=225): Observed M^+=225.1161; required 225.1154.

Photochemical reactions

Photochemical reactions: general procedure

The precursor was dissolved in acetonitrile (about 10 mL for 200 mg of the cyclopropylketone) and placed in pyrex tubes, then NEt_3 was added (5 mmol per each mmol of precursor) and the resulting mixture was purged with argon for about 10 min. The solution was then irradiated in a Rayonet apparatus fitted with 16 UV lamps showing an emission at 300 nm.

*Photochemical reaction of **6** to 8-propylidene-bicyclo [4.3.0] nonan-3-one (**8**).* Compound **6** (1.4 g, 22.6 mmol) and NEt_3 (3.08 g) in acetonitrile (80 mL) were irradiated for 6 days, the resulting solution was evaporated and the residue was purified using column chromatography

(cyclohexane/ethyl acetate 8:2) yielding 80 mg of unreacted starting material and the photoproduct **8** (405 mg, 29%) as an oil and as a mixture of 4 diastereoisomers (*cis/trans* 1:6 at the ring junction and unknown *cis/trans* ratio at the double bond). Spectroscopical data for compound **8**: - ^{1}H NMR ($CDCl_3$) δ 1.55 (br d, 3H, J=6.7Hz), series of multiplets between 1.2 and 2.7, 5.4 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.54 (CH_3), 29.61 (CH_2), 29.84 (CH_2), 34.06 (CH_2), 35.64 (CH_2), 38.47 (CH_2), 40.08 (CH_2), 41.07 (CH_2), 44.37 (CH), 44.43 (CH), 46.02 (CH), 47.30 (CH_2), 47.47 (CH_2), 116.26 (CH vinyl), 141.25, 211.42 (CO). IR 2940, 1722, 1439, 813 cm^{-1}. MS m/z = 164(33, M^+), 93(95), 79(97), 39(100). Anal. Calcd. for $C_{11}H_{16}O$ (M.W.=164): Observed M^+=164.1196; required 164.1201.

In an alternative experiment 280 mg (1.89 mmol) of **7**, 1.91 g (18.9 mmol) of TEA and 201 mg (1.91 mmol) of $LiClO_4$ were irradiated at 254 nm (quartz tubes) leading to **8** in 45% yield.

*Ozonolysis of compound **8** to trans-and cis-bicyclo[4.3.0]nonan-3,8-dione (**10**):* Ozone was bubbled for 20 min through a solution of 375 mg (2.3 mmol) of **8** dissolved in 40 mL of $MeOH/CH_2Cl_2$ 1:1 at -78 °C. After this time the solution became light blue and was stirred for additional 30 min at room temperature and then 460 μL of Me_2S were added. The solvents were removed and the crude residue was purified using column chromatography (cyclohexane/ethyl acetate 5:5) yielding 180 mg of pure *trans* isomer **10a** as a white solid (m.p. 92-94 °C) and 100 mg of a (1:1) mixture of the *cis* and *trans* isomers; 280 mg of product (80%).
*Spectroscopic data of **10a**:* - ^{1}H NMR ($CDCl_3$) δ 1.55 (m; 1H), 1.8-2.0 (m, 4H), 2.25 (m, 2H), 2.3-2.5 (m, 4H), 2.65 (br d, 1H, J=14Hz). ^{13}C NMR ($CDCl_3$) δ 29.73 (CH_2), 41.19 (CH_2), 42.03 (CH), 43.08 (CH), 44.46 (CH_2), 45.77 (CH_2), 46.75 (CH_2), 208.84 (CO), 215.75 (CO). IR 2960, 1756, 1708 cm^{-1}. MS m/z = 151 M^+-1(28), 39(100). Anal. Calcd. for $C_9H_{12}O_2$ (M.W.=152): C 71.05; H 7.89; found: C 69.89; H 8.01.
*Spectroscopic data of **10b** (from the mixture):* ^{13}C NMR ($CDCl_3$) δ 28.11 (CH_2), 34.34 (CH), 37.97 (CH), 38.45 (CH_2), 42.73 (CH_2), 42.93 (CH_2), 43.71 (CH_2), 210.75 (CO), 216.99 (CO).

*Photochemical reaction of compound 7 to 8-methylene-bicyclo[4.3.0]-nonan-3-one (**9**).* Compound **7** (320 mg, 2.2 mmol) and NEt_3 (1.1 g) in acetonitrile (25 mL) were irradiated for 6 days. The resulting solution was evaporated and the residue was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding firstly the intramolecular photoproduct **9** (66 mg, 20%) as an oil, which is a mixture *cis/trans* 1:6 (calculated from ^{13}C) and secondly 35 mg of unchanged starting material. - ^{1}H NMR ($CDCl_3$) δ 1.5 (m, 1H), 1.6-1.8 (m, 2H), 1.95 (m, 1H), 2.1 (m, 1H), 2.2 (m, 2H), 2.32 (m, 1H), 2.45 (m, 1H), 2.5-2.6 (m, 3H), 4.9 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 29.56 (CH_2), 38.06 (CH_2), 39.60 (CH_2), 41.02 (CH_2), 44.76 (CH), 46.31 (CH), 47.24 (CH_2), 44.76 (CH), 46.31 (CH), 47.24 (CH_2), 106.78 (CH_2 vin), 150.47, 211.47 (CO). IR 3077, 2935, 1720, 883 cm^{-1}. MS m/z = 150 M^+ (43), 91(91), 39(100). Anal. Calcd. for $C_{10}H_{14}O$ (M.W.=150): Observed M^+= 150.1037; required 150.1044.

*Photochemical reaction of compound **12** to 2-methylene-spiro[4.5]decan-7-one (**13**).* Compound **12** (625 mg, 3.86 mmol) and NEt_3 (1.95 g) in acetonitrile (45 mL) were irradiated for 4 days, the resulting solution was evaporated and the residue was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding first the intramolecular photoproduct **13**

(145 mg, 23%) as an oil and second 80 mg of unchanged starting material. - ^{1}H NMR ($CDCl_3$) δ 1.6 (m, 2H), 1.7 (m, 2H), 1.85 (m, 2H), 2.15 (m, 2H), 2.22 (s, 2H), 2.28 (t, 2H, J=7Hz), 2.34 (t, 2H, J=7Hz), 4.85 (br s, 2H). ^{13}C NMR ($CDCl_3$) δ 23.38 (CH_2), 30.23 (CH_2), 35.58 (CH_2), 37.44 (CH_2), 41.21 (CH_2), 45.42 (CH_2), 47.18, 52.10, (CH_2), 106.80 (CH_2 vinyl), 150.43, 211.42 (CO). IR 3077, 2949, 1720, 1437, 883 cm^{-1}. MS m/z = 163 M^+-1(1), 106(100). Anal. Calcd. for $C_{11}H_{16}O$ (M.W.=164): Observed M^+=164.1204; required 164.1201.

*Photochemical reaction of compound **17** to 8-methylene-bicyclo[4.3.0]nonan-2-one (**18**).* Compound **17** (1.46 g, 9.86 mmol) and NEt_3 (5.0 g) in acetonitrile (80 mL) were irradiated for 6 days, the resulting solution was evaporated and the residue was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding firstly the intramolecular photoproduct **18** (380 mg, 27%) as an oil and secondly 300 mg of unchanged starting material. - ^{1}H NMR ($CDCl_3$) δ 1.6 (m, 1H), 1.8 (m, 2H), 1.95 (m, 1H), 2.1-2.2 (m, 1H), 2.3-2.5 (m, 4H), 2.55 (m, 1H), 2.8 (m, 2H), 4.9 (s, 2H). ^{13} C NMR ($CDCl_3$) δ 23.96 (CH_2), 26.66 (CH_2), 33.41 (CH_2), 38.18 (CH_2), 39.33 (CH_2), 42.63 (CH), 52.87 (CH), 107.10 (CH_2 vinyl), 149.15, 212.97 (CO), IR 3070, 2940, 1711, 880 cm^{-1}. MS m/z = 150 M^+(39), 104(68), 79(100).

*Photochemical reaction of compound **25** to trans-3,4,4a,9,9a,10-hexahydro-2-(1H)-anthracenone (**28**).* Compound **25** (1.2 g, 6.0 mmol) and NEt_3 (3.04 g) in acetonitrile (70 mL) were irradiated for 5 days, the resulting solution was evaporated and the residue was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding as the first fraction the ring-opened photoproduct **30** (46 mg, 4%) as an oil, as the second fraction the intramolecular product **28** (94 mg, 8%) as a white solid (a small amount was crystallized from methanol m.p. 114-115 °C) and finally 200 mg of unchanged starting material.

*Data of **28**:* ^{1}H NMR ($CDCl_3$) δ 1.5 (m, 1H), 1.85 (m, 2H), 2.14 (dd, 1H, J=12.3Hz, J=13,8Hz), 2.20 (m, 1H), 2.4 (m, 3H), 2.5-2.6 (m, 2H), 2.82 (dd, 1H, J=4.8Hz, J=16.5Hz), 2.87 (dd, 1H, J=4.8Hz, J=16.5Hz), 7.00 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 33.47 (CH_2), 36.12 (CH_2), 37.28 (CH), 37.78 (CH_2), 39.74 (CH), 41.25 (CH_2), 47.92 (CH_2), 126.00 (CH), 128.70 (CH), 135.01, 135.67, 210.84 (CO). IR 2928, 1728, 748 cm^{-1}. MS m/z = 201 M^++1(42), 142(100). Anal. Calcd. for $C_{14}H_{16}O$ (M.W.=200): Observed M^+ 200.1201; required 200.1201.

*trans-3-Methyl-4-benzylcyclohexanone (**30**).* ^{1}H NMR ($CDCl_3$) δ 1.11 (d, 3H, J=6.5Hz), 1.3 (m, 1H), 1.64 (m, 1H), 1.74 (m, 1H), 1.86 (m, 1H), 2.1 (m, 1H), 2.18 (m, 1H), 2.22-2.32 (m, 2H), 2.4 (ddd, 1H, J=2Hz, J=4Hz, J=14Hz), 3.1 (dd, 1H, J=4Hz, J=14Hz), 7.0-7.2 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 20.65 (CH_3), 30.42 (CH_2), 38.08 (CH), 39.25 (CH_2), 40.67 (CH_2), 44.17 (CH), 49.03 (CH_2), 126.09 (CH), 128,39 (CH), 129.16 (CH), 140.52, 211.62 (CO), IR 2959, 1720, 745, 708 cm^{-1}. MS m/z = 202 M^+(64), 91(100). Anal. Calcd. for $C_{14}H_{18}O$ (M.W.=202): Observed M^+=202.1364; required 202.1358.

*Photochemical reaction of compound **26** to trans-3,4,4a,9,9a,10-hexahydro-7-methoxy-2-(1H)-anthracenone (**29**).* Compound **26** (1.2 g, 5.2 mmol) and NEt_3 (2.65 g) in acetonitrile (70 mL) were irradiated for 6 days, the resulting solution was evaporated and the residue was purified using column chromatography (cyclohexane/ethyl acetate 8:2) yielding as the first fraction the ring opened photoproduct **31** (28 mg, 2%) as an oil, as the second fraction the intramolecular

product **29** (63 mg, 5%) as a white solid (a small amount was crystallized from cyclohexane m.p. 148-149 °C) and finally 206 mg of unchanged starting material. - ^{1}H NMR ($CDCl_3$) δ 1.5 (m, 1H), 1.85 (m, 2H), 2.14 (dd, 1H, J=12.3Hz, J=13.8Hz), 2.20 (m, 1H), 2.4 (m, 3H), 2.5-2.6 (m, 2H) 2.82 (dd, 1H, J=4.8Hz, J=16.5Hz), 2.87 (dd, 1H, J=4.8Hz, J=16.5Hz), 3.8 (s, 3H), 6.6 (d, 1H, J=2.7Hz), 6.7 (dd, 1H, J=2.7Hz, J=8.3Hz), 6.98 (d, 1H, J=8.3Hz). ^{13}C NMR ($CDCl_3$) δ 33.44 (CH_2), 35.33 (CH_2), 37.49 (CH), 38.06 (CH_2), 39.68 (CH), 41.23 (CH_2), 47.87 (CH_2), 55.25 (CH_3), 112.34 (CH), 113.18 (CH), 127.80, 129.53 (CH), 136.09, 157.75, 210.86 (CO), IR 2946, 1718, 1506, 1271 cm^{-1}. MS m/z = 230 M^+(100). Anal. Calcd. for $C_{15}H_{18}O_2$ (M.W.=230): Observed M^+=230.1311; required 230.1307.

*trans-3-Methyl-4-(4-methoxybenzyl)cyclohexanone (**31**).* ^{1}H NMR ($CDCl_3$) δ 1.1 (d, 3H, J=6.5Hz), 1.3 (m, 1H), 1.75 (m, 1H), 1.9 (m, 1H), 2.1 (m, 1H), 2.2 (m, 1H), 2.25-2.35 (m, 2H), 2.4 (ddd, 1H, J=2Hz, J=4Hz, J=14Hz), 3.05 (dd, 1H, J=4Hz, J=14Hz), 6.85 (d, 2H, J=8.5Hz), 7.1 (d, 2H, J=8.5Hz). ^{13}C NMR ($CDCl_3$) δ 20.63 (CH_3), 30.36 (CH_2), 37.94 (CH), 38.07 (CH_2), 40.65 (CH_2), 44.25 (CH), 48.97 (CH_2), 55.27 (CH_3), 113.80 (CH), 130.01 (CH), 132.44, 158.00, 211.02 (CO). IR 2976, 1708, 1265 cm^{-1}. MS m/z=232M^+(100), 121(73). Anal. Calcd. for $C_{15}H_{20}O_2$ (M.W.=232): Observed M^+=232.1467; required 232.1463.

*Photochemical reaction of compound **27**.* Compound **27** (910 mg, 4.04 mmol) and NEt_3 (2.02 g) in acetonitrile (45 mL) were irradiated for 6 days but after this time only the starting material was recovered without detection of any photoproduct.

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