Photocycloaddition of Cyclohex-2-enones to 2-Methylbut-1-en-3-yne

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Irradiation (350 nm) of 2-alkynylcyclohex-2-enones **1** in benzene in the presence of an excess of 2-methylbut-1-en-3-yne (**2**) affords in each case a mixture of a *cis*-fused 3,4,4a,5,6,8a-hexahydronaphthalen-1(2*H*)-one **3** and a bicyclo[4.2.0]octan-2-one **4** (*Scheme 2*), the former being formed as main product *via* 1,6-cyclization of the common biradical intermediate. The (parent) cyclohex-2-enone and other alkylcyclohex-2-enones **7** also give naphthalenones **8**, albeit in lower yields, the major products being bicyclo[4.2.0]octan-2-ones (*Scheme 4*). No product derived from such a 1,6-cyclization is observed in the irradiation of 3-alkynylcyclohex-2-enone **9** in the presence of **2** (*Scheme 4*). Irradiation of the 2-cyano-substituted cyclohexenone **12** under these conditions again affords only traces of naphthalenone **13**, the main product now being the substituted bicyclo[4.2.0]oct-7-ene **16** (*Scheme 5*), resulting from [2 + 2] cycloaddition of the acetylenic C–C bond of **2** to excited **12**.

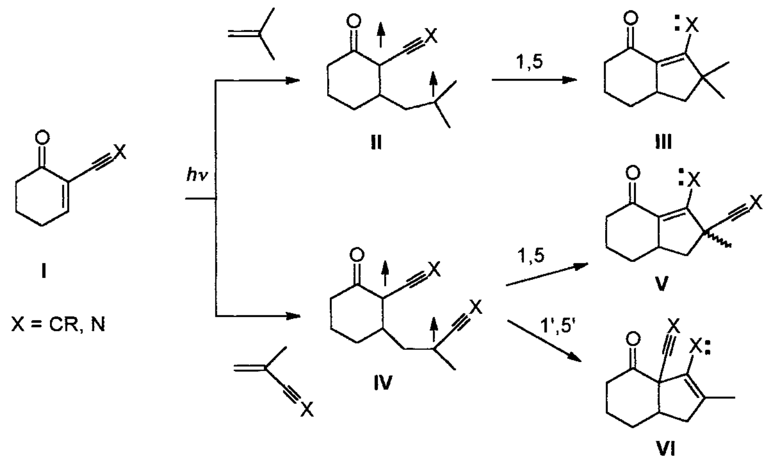
Introduction. – Triplet alkyl-propargyl (= alkyl-prop-2-ynyl) or alkyl-cyanoalkyl 1,4-biradicals undergo spin-selective 1,5-cyclization to vinylcarbenes and vinylnitrenes, respectively [1]. This is illustrated in the photocycloaddition of 2-alkynyl- or 2-cyano-substituted cyclohex-2-enones **I** to alkenes, *e.g.* 2-methylpropene, the corresponding cyclization **II** → **III** allowing the preparation of tricyclic furans [2] or isoxazoles [3] in good yields. In this context, it seemed interesting to generate and investigate triplet *bis-propargyl*, *cyano-alkylpropargyl*, or *bis-cyanoalkyl* 1,4-biradicals **IV**, as such transients should exhibit constitutional selectivity, *i.e.*, be able to undergo *two* differential 1,5-cyclizations to intermediates **V** and **VI**, respectively (*Scheme 1*). Here we report on the photocycloaddition of compounds **I** and of other cyclohex-2-enones to 2-methylbut-1-en-3-yne[1]).

Results. – Irradiation (λ 350 nm) of 2-alkynylcyclohex-2-enone **1a** in the presence of a tenfold molar excess of 2-methylbut-1-en-3-yne (**2**) in benzene affords two products in a 1:5 ratio (increasing retention times, monitoring by GC) which can be separated and isolated by liquid chromatography[1]). MS Analysis establishes that both are enone + enyne adducts. NMR Spectra confirm the main product **3a** to be a 3,4,4a,5,6,8a-hexahydro-6-methylidenenaphthalen-1(2*H*)-one, while a bicyclo[4.2.0]octan-2-one structure is assigned to the minor product **4a**[1]). We now found that cyclohexenones **1b** and **1c** behave like **1a**, affording a 10:3 mixture **3b**/**4b** and a 2:1 mixture **3c**/**4c**, respectively, and that for cyclohexenones **1d** and **1e**, the product ratio is roughly reversed, being 1:2 for **3d**/**4d** and 2:3 for **3e**/**4e**, respectively (*Scheme 2*).

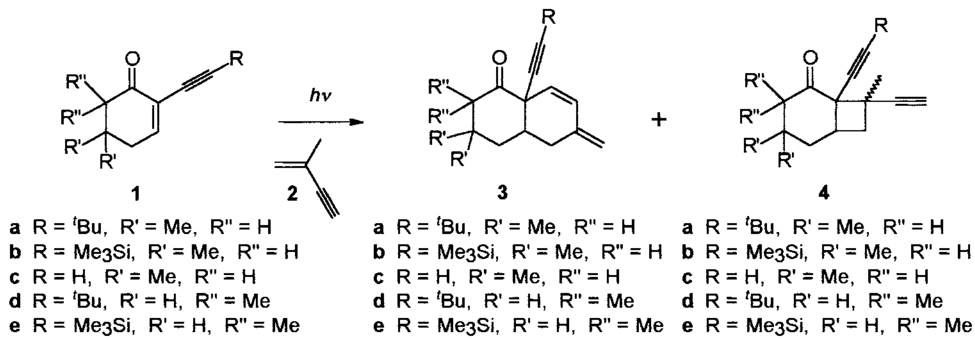
We had shown that irradiation of **1a** and **2** in MeOH affords a 1:1:2:2 mixture of **3a**, **4a**, and the two diastereoisomeric allyl ethers **5a** and **6a**[1]). We now found that

[1]) For preliminary results on the reaction of **1a** and **2**, see [4].

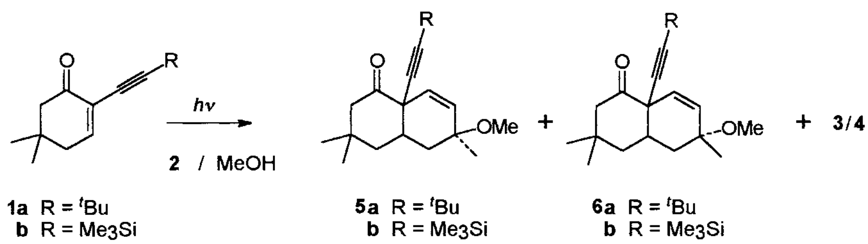
Scheme 1



Scheme 2



Scheme 3

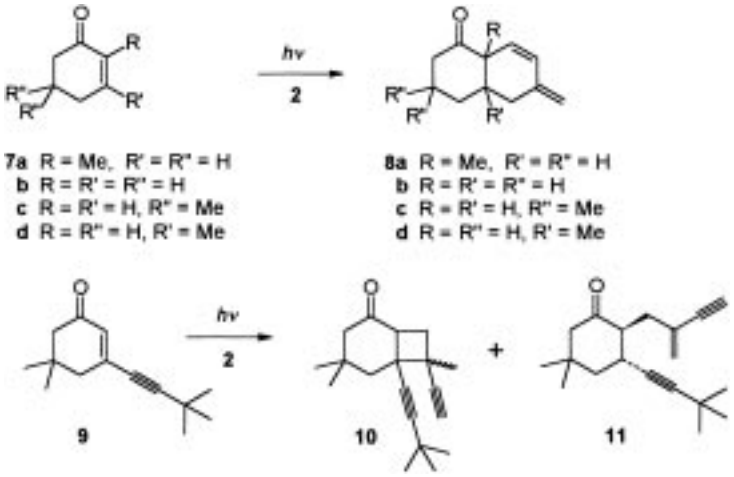


compound **1b** behaves similarly, giving a 2:2:3:3 mixture of **3b**, **4b**, **5b**, and **6b**, respectively (*Scheme 3*).

As the alkynyl side chain on C(2) of the cyclohexenone seems not necessarily to be involved in these reactions, other cyclohexenones **7** were investigated. First, we found that 2-methylcyclohex-2-enone (**7a**) gives naphthalenone **8a** preferentially (1.4:1) over a bicyclooctanone. The parent (unsubstituted) compound **7b** had been reported [5] to

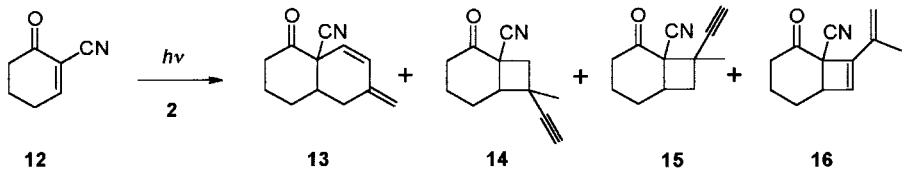
afford a mixture of six bicyclooctanones exclusively, but in our hands, GC/MS analysis of an irradiated mixture of **7a** and **2** does, indeed, indicate the formation of 7–8% naphthalenone **8b** besides the six [2+2] cycloadducts. Then we found that 5,5-dimethylcyclohex-2-enone (**7c**) yields 16% of **8c** and a mixture of five bicyclooctanones (84%). Surprisingly, even 3-methylcyclohex-2-enone (**7d**) gives naphthalenone **8d** (30%) in addition to 3 bicyclooctanones. Finally, irradiation of 3-alkynylcyclohex-2-enone **9** in the presence of **2** affords a 9:1 mixture of bicyclooctanone **10** and cyclohexanone **11** without any detectable traces of a naphthalenone (*Scheme 4*).

Scheme 4



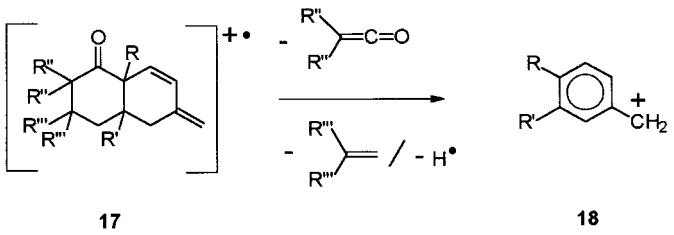
Irradiation of 6-oxocyclohexene-1-carbonitrile (**12**) in the presence of excess **2** affords a 1:1:1:3 mixture of enone + enyne adducts **13**–**16**. The three minor products are the expected ones, *i.e.* naphthalenone **13** and the regioisomeric bicyclooctane-1-carbonitriles **14** and **15**. Surprisingly, the main product **16** is now a bicyclooctene-1-carbonitrile, *i.e.*, a [2+2] photocycloadduct resulting from addition of the C≡C bond of **2** to the C=C bond of excited **12** (*Scheme 5*).

Scheme 5



Besides straightforward characterization by NMR spectroscopy, naphthalenones **3**, **8**, and **13** can be easily identified by their typical mass spectra. Except for trimethylsilyl derivatives **3b** and **3e**, which display base peaks at *m/z* 73 (Me_3Si^+), all other naphthalene derivatives exhibit preferential fragmentation of the molecular ion **17** by loss of two ring C_2 units (ketene or dimethylketene and ethene or 2-methylpropene) and a H-radical to give benzyl cation **18** (*Scheme 6*).

Scheme 6

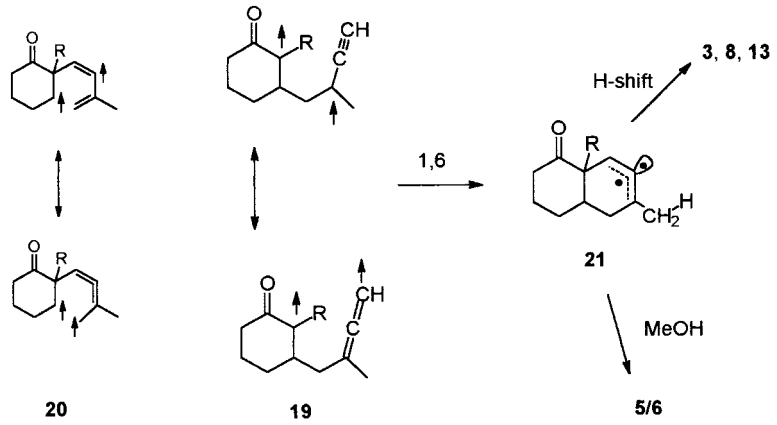


17 **18**

Discussion. – Besides affording both bicyclo[4.2.0]octan-2-ones and 1-oxaspiro[3.5]non-5-enes with alkenes [6] and bicyclo[4.2.0]oct-7-en-2-ones with alkynes [7], excited cyclohex-2-enones react with 2-methylbut-1-en-3-yne in a novel cyclohexaanellation to give 3,4,4a,5,6,8a-hexahydro-6-methylidenenaphthalen-1(2*H*)-ones.

Given the constitution of naphthalenones **3**, **8**, and **13**, it is evident that their formation requires 1,6-cyclization of either biradical **19** – formed by binding of the terminal olefinic C-atom of **2** to C(3) of the excited cyclohexenone – or biradical **20** (from binding of the terminal acetylenic C-atom of **2** to C(2) of the excited enone) (see *Scheme 7*). The following arguments favor the – selective – intermediacy of oxocyclohexylpropargyl biradical **19** in exclusion of that of **20**. First, all products formed in irradiations of compounds **1** and alkenes [1–3] arise from biradical precursors formed by bonding of the less substituted olefinic C-atom to C(3) of the enone. Furthermore, it is known [7] from irradiations of cyclohex-2-enones and terminal alkynes that head-to-head regioisomers, *i.e.*, those arising from bonding of the unsubstituted acetylenic C-atom to C(3) of the cyclohexenone, are formed preferentially or exclusively. This is reflected in the constitution of **16**, the only photocycloadduct arising from addition of the C≡C bond of **2** to the enone C=C bond. Finally, it has been established in competition experiments [8] that excited cyclohexenones react more efficiently with alkenes than with alkynes. Taking the

Scheme 7



20 **19** **21** **5/6**

intermediacy of biradical **19** in the formation of **3**, **8**, or **13** for granted, the next question thus regards the multiplicity of this species prior to 1,6-cyclization, the intermediate resulting from this step, and its final conversion to a 6-methylidenenaphthalen-1-one.

From detailed *ab initio* calculations on cyclohexa-1,2-diene [9][10], it results that *a*) the ground-state potential surface has a well-defined minimum corresponding to a chiral (C_2 symmetry) allenic structure, closely connected to species best described as biradicals, *b*) that these corresponding triplet and singlet biradicals are nearly isoenergetic, lying only 11 kcal/mol above the closed-shell ground state, and *c*) that zwitterionic structures correspond to excited states of this molecule. On the other hand, a less strained 1-methylcyclohepta-1,2-diene is known [11] to dimerize, but not to isomerize to a methylenecycloheptene. Putting these pieces of evidence together, the most probable path for the overall transformation of biradical **19** to the final product thus involves 1,6-cyclization on either triplet or singlet level to **21** with *concomitant* H-shift from the methyl group to the central allenic C-atom (formation of **3**, **8**, and **13**, resp.). In MeOH, trapping of **21** by the solvent (formation of allylic ethers **5**/**6**) intervenes (*Scheme 7*). Trapping of strained allenes by nucleophiles is a well-known process [12]. In naphthalenone **8c**, the two six-membered rings are unambiguously *cis*-fused (J(4a,8a) = 5 Hz), H–C(4a) being in the axial (J(4a,4ax) = 12.5 Hz) and H–C(8a) in the equatorial position (J(8a,2eq) = 2 Hz). From the fact that the H,H-coupling patterns for H–C(4), H–C(4a), and H–C(5) in all compounds **3**, **8**, and **13** are alike, it becomes evident that the ring fusion in all naphthalenones is *cis*.

It is noteworthy that no isomeric 3,4,4a,7,8,8a-hexahydro-7-methylidenenaphthalen-1(2*H*)-ones are formed at all from 3-alkynylcyclohexenone **9** and enyne **2**. This suggests that the carbonyl group adjacent to the (alkyl) radical center is necessary for this stepwise [4 + 2] cycloaddition of an enyne to a dienophile. Efficient formation of naphthalenones thus requires *a*) selective binding of the C(1) of the enyne at C(3) of the triplet-excited cyclohexenone and *b*) a conformation of biradical **19** wherein 1,6-cyclization is kinetically favored over either 1,4-cyclization or disproportionation to starting materials.

Finally, it is remarkable that on the one side the excited cyclohexenones **1**, **7**, and **9** cycloadd chemoselectively to the C=C bond of **2** to the exclusion of any cyclobutene formation, and that on the other side cyano-substituted cyclohexenone **12** and **2** give bicyclooctene **16** as the major (50%) photocycloadduct. From these results it seems reasonable to propose a mechanism involving an exciplex (as a precursor to bicyclooctanones and naphthalenones) in equilibrium with a contact ion pair (the precursor for the bicyclooctenone), the amount of the latter increasing with decreasing reduction potential of the (excited) cyclohexenone (*Scheme 8*). Such equilibria have been invoked to explain the formation of oxetanes in the photocycloaddition of cyclohexenones to tetramethoxyethylene [6] as well as the competing 1,2- *vs.* 1,3-photocycloaddition of arenes to alkenes [13].

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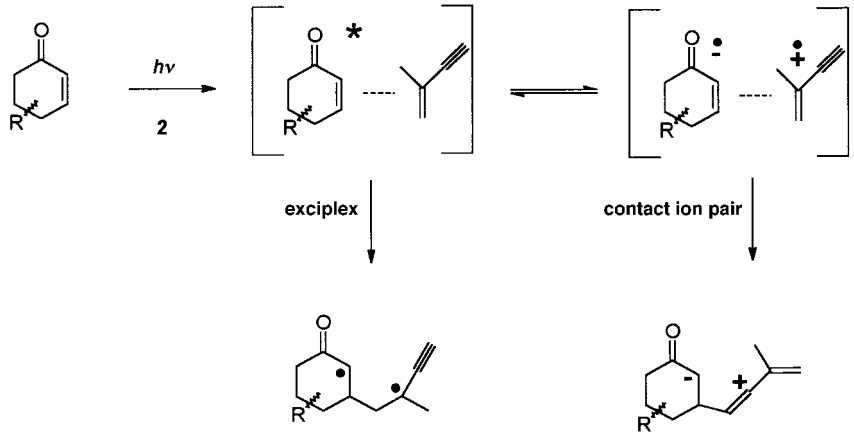
Scheme 8



Experimental Part

1. *General*. Photolyses: *Rayonet-RPR-100* photoreactor equipped with 350-nm lamps. GC: 30-m *SE-30* capillary column. UV Spectra: in nm (log ε). ^{1}H- and ^{13}C-NMR Spectra: at 500 and 125.8 MHz, resp.; chemical shifts in ppm rel. to $SiMe_4$ (=0 ppm), *J* in Hz. MS: at 70 eV; in *m/z* (rel. intensity in %).

2. *Starting Materials*. Alkynylcyclohexenones **1a**, **1d** [2], **1b**, **1e** [14], and **9** [15], cyclohexenones **7a** [16] and **7c** [17], oxocyclohexenecarbonitrile **12** [18], and enyne **2** [19] were synthesized according to the literature. Cyclohexenones **7b** and **7d** are commercially available.

5,5-Dimethyl-2-ethynylcyclohex-2-enone (**1c**) was obtained in analogy to [2] from 2-iodo-5,5-dimethylcyclohex-2-enone and ethynyltributylstannane in 41% yield. M.p. 54°, after purification by chromatography (SiO_2, pentane/Et_2O 6:1). UV (C_6H_{12}): 311 (1.998), 254 (3.748). ^{1}H-NMR ($CDCl_3$): 7.25 (*t*, *J* = 4.6); 3.09 (*s*), 2.36 (*s*, 2 H); 2.35 (*d*, *J* = 4.6, 2 H); 1.07 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 195.7 (*s*); 153.7 (*d*); 123.6 (*s*); 80.3 (*d*); 77.9 (*s*); 51.4 (*t*); 40.4 (*t*); 33.9 (*s*); 28.3 (*q*). MS: 148 (34, M^+), *92*.

3. *Photolyses*. 3.1. *General Procedures*. In prep. exper., an Ar-degassed soln. of cyclohexenone (1 mmol) and **2** (10 mmol) in benzene (20 ml) was irradiated for 9–16 h (GC monitoring) until total conversion of the enone was achieved. After evaporation, the residue was worked up by chromatography (CC) on SiO_2.

In anal. exper. (anal.), Ar-degassed solns. of cyclohexenone (0.1 mmol) and **2** (1 mmol) in benzene (2 ml) were irradiated for 1–2 h, and the mixture was analyzed by GC/MS and ^{1}H-NMR.

3.2. **1a** *in Benzene* (prep.). CC (pentane/AcOEt 6:1) of **3a**/**4a** afforded first 183 mg (68%) of **3a** and then 13 mg (5%) of **4a**.

cis-*8a-(3,3-Dimethylbut-1-ynyl)-3,4,4a,5,6,8a-hexahydro-3,3-dimethyl-6-methylidenenaphthalen-1(2*H*)-one* (**3a**): Colorless oil. R_f 0.27. ^{1}H- and ^{13}C-NMR [4]. MS: 270 (75, M^+), 171 (53), *157*.

1-(3,3-Dimethylbut-1-ynyl)-8-ethynyl-4,4,8-trimethylbicyclo[4.2.0]octan-2-one (**4a**): One diastereoisomer. Colorless oil. R_f 0.24. ^{1}H- and ^{13}C-NMR [4]. MS: 270 (4, M^+), *105*.

3.3. **1b** *in Benzene* (prep.). CC (CH_2Cl_2/pentane 9:1) of **3b**/**4b** 10:3 afforded first 165 mg (57%) of **3b** and then 20 mg (7%) of **4b**.

cis-*3,4,4a,5,6,8a-Hexahydro-3,3-dimethyl-6-methylidene-8a-[(trimethylsilyl)ethynyl]naphthalen-1(2*H*)-one* (**3b**). Colorless oil. R_f 0.60. ^{1}H-NMR ($CDCl_3$): 6.25 (*d*, *J* = 9.7); 5.40 (*dd*, *J* = 1.0, 9.7); 5.03 (*s*); 5.01 (*d*, *J* = 1.0); 2.96 (*dd*, *J* = 4.5, 15.0); 2.51 (*dddd*, *J* = 3.5, 4.5, 4.5, 12.8); 2.32 (*d*, *J* = 13.2); 2.21 (*dd*, *J* = 3.5, 15.0); 2.12 (*dd*, *J* = 2.5, 12.8); 1.55 (*dd*, *J* = 12.8, 13.2); 1.34 (*ddd*, *J* = 2.5, 4.5, 13.2); 0.99 (*s*, 3 H); 0.95 (*s*, 3 H); 0.16 (*s*, 9 H). MS: 286 (6, M^+), 187 (4), *73*.

8-Ethynyl-4,4,8-trimethyl-1-[(trimethylsilyl)ethynyl]bicyclo[4.2.0]octan-2-one (**4b**): One diastereoisomer. Colorless oil. R_f 0.48. ^{1}H-NMR ($CDCl_3$): 272 (*dddd*, *J* = 3.0, 8.1, 9.2, 12.2); 2.42 (*dd*, *J* = 9.2, 11.7); 2.40 (*d*, *J* = 17.8); 2.39 (*s*); 2.33 (*dd*, *J* = 2.5, 17.8); 1.98 (*dd*, *J* = 3.0, 11.7); 1.92 (*dd*, *J* = 12.2, 13.7); 1.85 (*ddd*, *J* = 2.5, 9.2, 13.7); 1.52 (*s*, 3 H); 1.04 (*s*, 3 H); 0.96 (*s*, 3 H); 0.16 (*s*, 9 H). MS: 286 (0.1, M^+), *73*.

3.4. **1a** *in Methanol* (prep.). CC (pentane/AcOEt 6:1) of **3a**/**4a**/**5a**/**6a** 1:1:2:2 afforded **3a**, **4a**, then 45 mg (15%) of **5a**, and finally 36 mg (12%) of **6a**.

(4aα,6α,8aα)-8a-(3,3-Dimethylbut-1-ynyl)-3,4,4a,5,6,8a-hexahydro-6-methoxy-3,3,6-trimethylnaphthalen-1(2H)-one (**5a**): Colorless oil. R_f 0.20. ^{1}H- and ^{13}C-NMR [4]. MS: 302 (1, M^+), *98*.

(4aα,6β,8aα)-8a-(3,3-Dimethylbut-3-ynyl)-3,4,4a,5,6,8a-hexahydro-6-methoxy-3,3,6-trimethylnaphthalen-1(2H)-one (**6a**): Colorless oil. R_f 0.15. ^{1}H- and ^{13}C-NMR [4]. MS: 302 (0.1, M^+), *58*.

3.5. **1b** *in Methanol* (prep.). CC (CH_2Cl_2/pentane 9:1) of **3b**/**4b**/**5b**/**6b** 2:2:3:3 afforded **3b**, **4b**, then 35 mg (11%) of **5b**, and finally 25 mg (8%) of **6b**.

(4aα,6α,8aα)-3,4,4a,5,6,8a-Hexahydro-6-methoxy-3,3,6-trimethyl-8-[(trimethylsilyl)ethynyl]naphthalen-1(2H)-one (**5b**): Colorless oil. R_f 0.37. ^{1}H-NMR (C_6D_6): 5.94 (*d*, *J* = 10.0); 5.60 (*d*, *J* = 10.0); 3.05 (*s*, 3 H); 3.01 (*d*, *J* = 12.6); 2.94 (*dddd*, *J* = 3.2, 5.0, 5.7, 11.0); 2.15 (*dd*, *J* = 1.5, 12.7); 2.09 (*dd*, *J* = 5.7, 13.9); 1.99 (*dd*, *J* = 11.0, 13.9); 1.49 (*dd*, *J* = 3.2, 13.9); 1.32 (*ddd*, *J* = 1.5, 5.0, 13.2); 1.08 (*s*, 3 H); 0.81 (*s*, 3 H); 0.79 (*s*, 3 H); 0.12 (*s*, 9 H). MS: 318 (0.1, M^+), *73*.

(4aα,6β,8aα)-3,4,4a,5,6,8a-Hexahydro-6-methoxy-3,3,6-trimethyl-8-[(trimethylsilyl)ethynyl]naphthalen-1(2H)-one (**6b**): Colorless oil. R_f 0.29. ^{1}H-NMR (C_6D_6): 5.70 (*d*, *J* = 10.0); 5.64 (*d*, *J* = 10.0); 3.01 (*s*, 3 H); 2.61 (*d*, *J* = 12.6); 2.49 (*dddd*, *J* = 3.6, 5.1, 8.0, 8.5); 2.05 (*dd*, *J* = 1.5, 12.7); 1.97 (*dd*, *J* = 8.0, 13.9); 1.78 (*dd*, *J* = 8.5, 13.9); 1.72 (*dd*, *J* = 3.5, 13.9); 1.32 (*ddd*, *J* = 1.5, 8.0, 13.2); 1.12 (*s*, 3 H); 0.79 (*s*, 3 H); 0.78 (*s*, 3 H); 0.16 (*s*, 9 H). MS: 318 (0.5, M^+), *73*.

3.6. **1c** *in Benzene* (anal.). A 2:1 mixture of **3c** (MS: 214 (4, M^+), *115*) and **4c** (MS: 214 (0.1, M^+), *52*) was obtained.

3.7. **1d** *in Benzene* (anal.). A 1:2 mixture of **3d** (MS: 270 (6, M^+), 171 (77), *157*) and **4d** (MS: 270 (0.1, M^+), *57*) was obtained.

3.8. **1e** *in Benzene* (anal.). A 2:3 mixture of **3e** (MS: 286 (6, M^+), 171 (10), *73*) and **4e** (MS: 286 (5, M^+), *73*) was obtained.

3.9. **7a** *in Benzene* (prep.). CC (CH_2Cl_2/pentane 9:1) of the 3:2 mixture of **8a** and one cyclobutane adduct afforded first 59 mg (30%) of cis-*3,4,4a,5,6,8a-hexahydro-8a-methyl-6-methylidenenaphthalen-1(2H)-one* (**8a**). Colorless oil. R_f 0.55. ^{1}H-NMR (C_6D_6): 6.01 (*d*, *J* = 9.7); 5.30 (*dd*, *J* = 1.0, 9.7); 4.83 (*s*); 4.78 (*d*, *J* = 1.0); 2.30 (*dd*, *J* = 4.1, 15.3); 2.16 (*ddd*, *J* = 1.5, 10.2, 14.0); 2.08 (*m*, 1 H); 1.92 (*dd*, *J* = 5.1, 15.3); 1.56 (*dddd*, *J* = 3.6, 4.1, 5.1, 13.7); 1.48 (*m*, 1 H); 1.36 (*m*, 1 H); 1.31 (*m*, 1 H); 1.29 (*m*, 1 H); 1.20 (*s*, 3 H). MS: 176 (27, M^+), *105*.

3.10. **7b** *in Benzene* (anal.). Monitoring by GC indicated the formation of six bicyclooctanones [5] and 7% of **8b** with slightly higher retention time. MS: 162 (20, M^+), *91*.

3.11. **7c** *in Benzene* (prep.). The 1:6 mixture of **8c** and five bicyclooctanones was separated by CC (CH_2Cl_2/pentane 9:1) to afford first 17 mg (9%) of cis-*3,4,4a,5,6,8a-hexahydro-3,3-dimethyl-6-methylidenenaphthalen-1(2H)-one* (**8c**). Colorless oil. R_f 0.11. ^{1}H-NMR (C_6D_6): 6.06 (*dd*, *J* = 3.1, 9.7); 5.22 (*dd*, *J* = 1.0, 9.7); 4.83 (*s*); 4.79 (*d*, *J* = 1.0); 3.06 (*m*, 1 H); 2.16 (*dd*, *J* = 4.1, 14.2); 2.03 (*d*, *J* = 13.2); 1.99 (*ddddd*, *J* = 3.1, 3.1, 4.1, 4.1, 12.1); 1.92 (*ddd*, *J* = 2.0, 2.5, 13.2); 1.89 (*dd*, *J* = 4.1, 14.2); 1.45 (*dd*, *J* = 12.1, 13.2); 1.00 (*s*, 3 H); 0.91 (*s*, 3 H); 0.85 (*ddd*, *J* = 2.0, 3.1, 13.2). MS: 190 (11, M^+), *91*.

3.12. **7d** *in Benzene* (prep.). The 2:5 mixture of **8d** and three bicyclooctanones was separated by CC (CH_2Cl_2/pentane 9:1) to afford first 20 mg (11%) of cis-*3,4,4a,5,6,8a-hexahydro-4a-methyl-6-methylidenenaphthalen-1(2H)-one* (**8d**). Colorless oil. R_f 0.49. ^{1}H-NMR (C_6D_6): 6.10 (*dd*, *J* = 2.0, 9.7); 5.41 (*dd*, *J* = 3.6, 9.7); 4.85 (*s*); 4.76 (*s*); 2.59 (*m*, 1 H); 2.05 (*m*, 1 H); 1.95 (*m*, 1 H); 1.93, 1.71 (*AB*, *J* = 14.2); 1.44 (*m*, 1 H); 1.35 (*m*, 1 H); 0.91 (*m*, 1 H); 0.75 (*s*, 3 H). MS: 176 (30, M^+), 105 (77), *91*.

3.13. **9** *in Benzene* (prep.). CC (pentane/AcOEt 6:1) of **10**/**11** 9:1 afforded first 8 mg (3%) of **11** and then 180 mg (66%) of **10**.

trans-*3-(3,3-Dimethylbut-1-ynyl)-5,5-dimethyl-2-(2-methylidenebut-3-ynyl)cyclohexan-1-one* (**11**): Light yellow oil. R_f 0.56. ^{1}H-NMR ($CDCl_3$): 5.49 (*s*); 5.46 (*s*); 3.15 (*m*, 1 H); 2.85 (*s*); 2.72 (*m*, 1 H); 2.56 (*m*, 2 H); 2.24; 2.20 (*AB*, *J* = 12.9); 1.86 (*dd*, *J* = 4.7, 13.9); 1.81 (*dd*, *J* = 5.1, 13.9); 1.17 (*s*, 9 H); 1.16 (*s*, 3 H); 1.01 (*s*, 3 H). MS: 270 (3, M^+), *131*.

6-(3,3-Dimethylbut-1-ynyl)-7-ethynyl-4,4,7-trimethylbicyclo[4.2.0]octan-2-one (**10**). One diastereoisomer. Colorless oil. R_f 0.52. ^{1}H-NMR (C_6D_6): 3.00 (*dd*, *J* = 10.0, 10.2); 2.35 (*d*, *J* = 14.2); 2.21 (*dd*, *J* = 10.0, 11.4); 2.09 (*d*, *J* = 14.5); 2.05 (*d*, *J* = 14.5); 1.98 (*s*); 1.93 (*d*, *J* = 14.2); 1.80 (*dd*, *J* = 10.2, 11.4); 1.48 (*s*, 3 H); 1.08 (*s*, 9 H); 1.07 (*s*, 3 H); 0.83 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 209 (*s*); 94 (*s*); 87 (*s*); 82 (*s*); 72 (*d*); 51 (*q*); 47 (*d*); 45 (*t*); 43 (*s*); 38 (*s*); 36 (*t*); 35 (*s*); 32 (*t*); 31 (*q*); 28 (*s*); 27 (*q*); 25 (*q*). MS: 270 (9, M^+), *148*.

3.14. **12** *in Benzene* (prep.). CC (Et_2O/pentane 3:1) of **13**–**16** 1:1:1:3 afforded first 12 mg (7%) of **14**, then 11 mg (6%) of **15**, 41 mg (22%) of **16**, and finally 8 mg (2%) of **13**/**16** 1:1.

7-Ethynyl-7-methyl-2-oxobicyclo[4.2.0]octane-1-carbonitrile (**14**): One diastereoisomer. Colorless oil. R_f 0.40. ^{1}H-NMR (C_6D_6): 2.62, 1.97 (*AB*, *J* = 12); 2.37 (*ddd*, *J* = 7.6, 12.0, 14.6); 2.24 (*dd*, *J* = 6.0, 8.0); 1.82 (*s*); 1.77–0.98 (*m*, 5 H); 1.07 (*s*, 3 H). MS: 187 (4, M^+), *66*.

8-Ethynyl-8-methyl-2-oxobicyclo[4.2.0]octane-1-carbonitrile (**15**): One diastereoisomer. Colorless oil. R_f 0.36. ^{1}H-NMR (C_6D_6): 2.44 (*dddd*, *J* = 5.5, 6.0, 6.5, 9.2); 2.25 (*ddd*, *J* = 5.5, 7.0, 18.3); 1.97 (*s*); 1.91 (*ddd*, *J* = 5.5, 8.5, 18.3); 1.73 (*dd*, *J* = 9.2, 12.3); 1.69 (*dd*, *J* = 6.0, 12.3); 1.47 (*s*, 3 H); 1.46 (*m*, 1 H); 1.10 (*m*, 2 H); 1.03 (*m*, 1 H). ^{13}C-NMR (C_6D_6): 200 (*s*); 118 (*s*); 85 (*s*); 75 (*d*); 52 (*s*); 39 (*t*); 37 (*t*); 37 (*s*); 36 (*d*); 28 (*q*); 26 (*t*); 19 (*t*). MS: 187 (4, M^+), *66*.

8-(1-Methylethenyl)-2-oxobicyclo[4.2.0]oct-7-ene-1-carbonitrile (**16**): Colorless oil. R_f 0.30. ^{1}H-NMR (C_6D_6): 5.63 (*s*); 5.34 (*d*, *J* = 1.5); 4.84 (*s*); 3.00 (*ddd*, *J* = 1.0, 1.5, 5.5); 2.05 (*ddd*, *J* = 3.2, 6.6, 18.9); 1.71 (*ddd*, *J* = 7.9, 11.0, 18.9); 1.45 (*s*, 3 H); 1.15 (*m*, 1 H); 1.06 (*m*, 1 H); 0.92 (*m*, 1 H); 0.87 (*ddd*, *J* = 4.0, 5.0, 14.0). ^{13}C-NMR (C_6D_6): 201 (*s*); 143 (*s*), 138 (*s*); 134 (*d*); 117 (*t*); 117 (*s*); 52 (*s*); 46 (*d*); 38 (*t*); 25 (*t*); 18 (*t*); 17 (*q*). MS: 187 (38, M^+), *116*.

*1,5,6,7,8,8a-Hexahydro-2-methylidene-5-oxonaphthalene-4a(2*H*)-carbonitrile* (**13**) (data of **13** from **13**/**16** 1:1): R_f 0.28. ^{1}H-NMR (C_6D_6): 5.88 (*d*, *J* = 9.5); 5.00 (*d*, *J* = 9.5); 4.71 (*s*); 4.66 (*s*); 2.50 (*dd*, *J* = 4.0, 15.0); 2.15 (*ddd*, *J* = 1.5, 10.2, 14.0); 2.07 (*m*, 1 H); 1.91 (*dd*, *J* = 5.1, 15.3); 1.80 (*dddd*, *J* = 3.6, 4.1, 5.1, 13.7); 1.55 (*m*, 1 H); 1.40 – 1.25 (*m*, 3 H). MS: 187 (20, M^+), *116*.

REFERENCES

[1] W. C. Agosta, P. Margaretha, *Acc. Chem. Res.* **1996**, *29*, 179.
[2] P. Margaretha, S. Reichow, W. C. Agosta, *J. Org. Chem.* **1994**, *59*, 5393.
[3] S. Andresen, P. Margaretha, *J. Photochem. Photobiol. A* **1998**, *112*, 135.
[4] B. Witte, P. Margaretha, *Org. Letters* **1999**, *1*, 173.
[5] A. Margaryan, E. P. Serebryakov, V. F. Kucherow, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, *25*, 840.
[6] G. Cruciani, H. J. Rathjen, P. Margaretha, *Helv. Chim. Acta* **1990**, *73*, 856.
[7] P. Margaretha, in 'Methods of Organic Chemistry (Houben-Weyl)', Vol. E17f, Ed. A. de Meijere, G. Thieme, Stuttgart, 1997, p. 656.
[8] P. de Mayo, M. C. Usselman, *Anal. R. Soc. Esp. Fis. Quim., Ser. B* **1972**, *68*, 779.
[9] M. W. Schmidt, R. O. Angus Jr., R. P. Johnson, *J. Am. Chem. Soc*. **1982**, *104*, 6838.
[10] R. O. Angus Jr., M. W. Schmidt, R. P. Johnson, *J. Am.Chem. Soc*. **1985**, *107*, 532.
[11] D. Venugopal, L. D. Todaro, P. Margaretha, W. C. Agosta, *Chem. Commun*. **1993**, 1014.
[12] A. T. Bottini, F. P. Corson, R. Fitzgerald, K. A. Frost Jr., *Tetrahedron* **1972**, *28*, 4883.
[13] J. Mattay, *Synthesis* **1989**, 233.
[14] B. Sander, S. Andresen, S. Reichow, K. Dubois, W. C. Agosta, P. Margaretha, *Helv. Chim. Acta* **1996**, *79*, 1428.
[15] H. J. Rathjen, P. Margaretha, S. Wolff, W. C. Agosta, *J. Am. Chem. Soc*. **1991**, *113*, 3904.
[16] E. W. Warnhoff, D. G. Martin, W. S. Johnson, 'Org. Synth., Coll. Vol. IV', Wiley, New York, 1963, p. 162.
[17] W. F. Gannon, H. O. House, 'Org. Synth., Coll. Vol. V', Wiley, New York, 1973, p. 294.
[18] F. F. Fleming, A. Huang, V. A. Sharief, Y. Pu, *J. Org. Chem*. **1997**, *62*, 3036.
[19] E. Defranq, T. Zesiger, R. Tabacchi, *Helv. Chim. Acta* **1993**, *76*, 425.

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