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Photochemical Behaviour of 4-Methylene-2-adamantanone, an Exocyclic *β,γ*-Unsaturated Ketone

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The photochemistry of 4-methylene-2-adamantanone (**1**) was studied in different solvents and under direct and sensitized irradiation. Depending on the conditions, *β,γ*-unsaturated ketone **1** underwent reactions characteristic of isolated ketones or alkenes. Direct irradiation of **1** in benzene afforded a mixture of 2-methylenenoradamantane (**11**) and 4-methylenebicyclo[3.3.1]-non-2-en-7-carbaldehyde (**12**). Irradiation of **1** in benzene in the presence of benzophenone gave oxetanes **10**, while the major products in acetone sensitized photolysis were identified as *syn*- and *anti*-4-(3-oxobutyl)-2-adamantanones (**8**). In protic solvent (ethanol), **1** reacted smoothly to give ketal **13**. The photochemical reactions that proceed through intramolecular interactions were not observed.

INTRODUCTION

In view of our continuing interest on the synthesis of the polycyclic strained carbocycles[1] by the oxa-di-*π*-methane rearrangement (ODPM), we turned our attention to 4-methylene-2-adamantanone (**1**) as a model system. It is known that *β,γ*-unsaturated carbonyl compounds may undergo several types of photoreactions:[2] the carbonyl reactions (*α*-cleavage, *γ*-hydrogen transfer, reduction, *etc.*), the olefin reactions (cycloadditions, *cis-trans*-isomerizations, reduction, *etc.*) and the bischromophoric reactions (ODPM rearrangement, 1,3-acyl shift, intramolecular oxetane formation, *etc.*). In bischromophoric system **2**, in which the double bond was incorporated into four- and five-mem-

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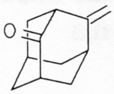
+ Permanent address: University of Zagreb, Faculty of Chemical Engineering and Technology, Department of Organic Chemistry, Marulićev trg 20, 41000 Zagreb, Croatia bered rings, the oxa-di-π-methane rearrangement was observed[3] under the acetone sensitization, but not in the six-membered ring. The ODPM rearrangement was also found in tricyclic systems **3**[1] and **4**[4] with the olefinic moiety incorporated into a five- and a six-membered ring as well as in system **7**, in which the double bond is a part of a six-membered ring and *exo*-positioned to the carbonyl group.[5] In contrast, the photolysis of methylene-cyclohexanone **6** gave, upon sensitized irradiation, only *cis-trans* isomerization.[6] In the case of 4-methylene-2-protoadamantanone (**5**), the acetone addition and rearrangement to adamantanone derivative was the reaction of priority.[7]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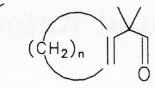

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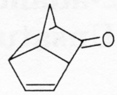
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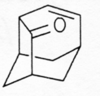
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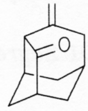
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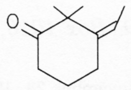
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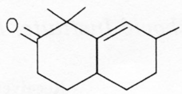
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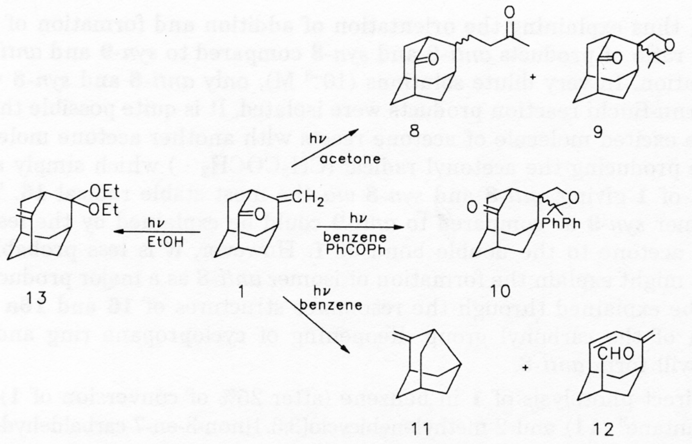
We now report the photochemical behaviour of 4-methylene-2-adamantanone (**1**), a tricyclic, rather rigid, compound with the β,γ-*exo*-double bond, in different solvents and under direct and sensitized irradiation (Scheme 1).

RESULTS AND DISCUSSION

4-Methylene-2-adamantanone (**1**) was synthesized according to literature procedure.[8] UV spectrum of unsaturated ketone **1** revealed enhanced n→π^* absorption [λ_{max}(EtOH/nm) 293 (ε = 105) towards 2-adamantanone [λ_{max}(EtOH/nm) 286 (ε = 20)], which suggests interaction between the two chromophores that might lead to intramolecular photochemical reactions.

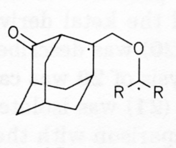
Irradiation of 4-methylene-2-adamantanone (**1**) in acetone solution gave, besides some unidentified polymers, four products, *anti*-**8**, *syn*-**8**, *syn*-**9** and *anti*-**9** in 40% yield and in the ratio 7.9 : 3.7 : 2.3 : 1, respectively. Mass spectrometry and elemental analyses established that all four products had the same molecular formula $C_{14}H_{20}O_2$. These data, as well as the absence of characteristic methylene protons in ^{1}H NMR spectra at 4.64 ppm, suggested formation of different isomeric products of acetone addition to the double bond. The IR spectrum of compounds *anti*-**8** and *syn*-**8** showed a band at 1720 cm^{-1} ascribed to the carbonyl groups which are well resolved in ^{13}C NMR spectrum and appear at 217.9 and 208.4 ppm. In ^{1}H NMR spectrum of *anti*-**8** and *syn*-**8** only, one singlet at 2.13 (*anti*-**8**) and 2.15 (*syn*-**8**) was found and assigned to methyl protons of *anti*- and *syn*-3-oxobutyl groups of *anti*- and *syn*-4-(3-oxobutyl)-2-adamantanones (**8**). The structure of the products was confirmed by the Wolff-Kishner reduction of the mixture of isomers, which gave only one product, 2-(*n*-butyl)adamantane (**14**). The spectral data for minor products *syn*-**9** and *anti*-**9** are consistent with the cycloadducts arising from a Paterno-Büchi reaction of acetone addition. The ^{13}C NMR spectra of the enriched mixture of *syn*-**9** and *anti*-**9** showed peaks at 216.17 and 217.09,



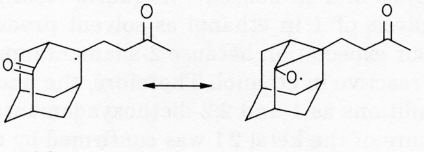
Scheme 1.

characteristic of carbonyl groups and signals at 88.07(s) and 88.29(s), as well as at 74.54(t) and 74.49(t), characteristic of C_2, and C_4, of the oxetane ring, respectively. Configuration of the obtained *syn*- and *anti*-spirooxetane **9** resulted from ^1H NMR: two doublets at 4.40 and 4.21 ppm for CH_2 protons of oxetane ring in *anti*-**9** as well as the methyl protons of oxetane ring in *syn*-**9** are deshielded due to the anisotropic effect of carbonyl group as compared to the same protons in *syn*-**9** and *anti*-**9**, respectively.

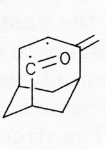
Irradiation of **1** in benzene in the presence of benzophenone as sensitizer, under conditions in which only excitation of the sensitizer was ensured (λ 350 nm), gave *syn*- and *anti*-spirooxetanes **10** (Scheme 1). After shorter irradiation time (40% of conversion), only *syn*-isomer **10** was isolated whereas upon longer irradiation (90% of conversion of **1**) also a small amount of *anti*-isomer **10** was observed,* in addition to a large amount of polymeric material.



15 R = CH_3
R = Ph



16 16a



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It is obvious that no energy transfer occurred under sensitization with acetone or benzophenone. The reactions involve the n→π* triplet state of the carbonyl moiety of acetone or benzophenone which adds to the double bond of **1** *via* the most stable

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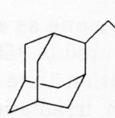
[*] ^1H NMR spectrum of crude reaction mixture showed two doublets at 4.62 and 4.35 ppm, which correspond to the protons at C_4, of the oxetane ring.

biradical **15**, thus explaining the orientation of addition and formation of products **9** and **10**. The ratio of products *anti*-**8** and *syn*-**8** compared to *syn*-**9** and *anti*-**9** depends on concentration. In very dilute solutions (10^{-3} M), only *anti*-**8** and *syn*-**8** were found and no Paterno-Büchi reaction products were isolated. It is quite possible that in dilute solutions the excited molecule of acetone reacts with another acetone molecule in the ground state producing the acetonyl radical ($CH_3COCH_2\cdot$) which simply adds to the double bond of **1** giving *anti*-**8** and *syn*-**8** *via* the most stable radical **16**. The higher yield on isomer *syn*-**9** as compared to *anti*-**9** could be explained by the less hindered approach of acetone to the double bond of **1**. However, it is less probable that the steric effects might explain the formation of isomer *anti*-**8** as a major product *vs.* *syn*-**8**. This might be explained through the resonance structures of **16** and **16a** due to the participation of the carbonyl group. Reopening of cyclopropane ring and hydrogen abstraction will form *anti*-**8**.

In the direct photolysis of **1** in benzene (after 25% of conversion of **1**), 2-methylenenoradamantane[9] (**11**) and 2-methylenebicyclo[3.3.1]non-3-en-7-carbaldehyde (**12**) were obtained in the ratio 1.4 : 1 by the Norrisch Type 1 process. Initial cleavage of the carbonyl-carbon bond gives the biradical **17** which can undergo stabilization by two routes: i) decarbonylation and recombination of the formed biradical to **11** and ii) intramolecular hydrogen abstraction to give **12**. After prolonged irradiation (90% of conversion of **1**), two other products appeared on account of **12**, showing that **12** is the primary product, which either thermally decomposes or undergoes further photoreaction. It is most likely that these two products found in the crude reaction mixture are the oxetanes* **18** and **19** formed from **12** by intramolecular 2+2 cycloaddition reaction.[10–13]



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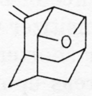

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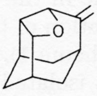

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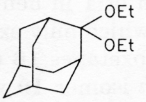

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In the direct photolysis of **1** in benzene, in quartz vessel, no product was detected.** However, the photolysis of **1** in ethanol as solvent produced the ketal derivative **13**. It was contrary to our expectation because 2-adamantanone (**20**) was described[14] to be photochemically unreactive in ethanol. Therefore, the photolysis of **20** was carried out under the same conditions as **1** and 2,2-diethoxyadamantane (**21**) was isolated in 40% yield.*** The structure of the ketal **21** was confirmed by comparison with the authentic sample obtained by acid-catalyzed synthesis.

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* The structures of **12**, **18** and **19** are proposed on the basis of GC-MS analysis as well as the ^{13}C NMR spectra of crude reaction mixtures obtained by work up after 25% and 90% of conversion of **1** (**12**: ^{13}C NMR δ: 202.65, 147.29, 133.75, 131.38, 112.87; **18**: ^{13}C NMR δ: 151.18, 102.43, 83,10; ^{13}C NMR δ: 153.16, 108.07, 87.53, 81.88). For comparison see Ref. 13.

** The course of reaction, followed by GC, showed disappearance of starting material and formation of some unidentified high molecular weight decomposition products.

*** All glassware were carefully base treated prior to use to avoid acid-catalyzed reaction. In addition, in the control experiment which was done in the dark under the same conditions for 48 hours **20** was completely unreactive.

In conclusion, the results presented in this work clearly show that 4-methylene-2-adamantanone (**1**), a tricyclic β,γ-unsaturated ketone, undergoes photochemical reactions characteristic of isolated ketones or alkenes. Oxa-di-π-methane rearrangement is not observed although, according to the enhanced $n \rightarrow \pi^*$ absorption, the bischromophoric reaction could be expected.

EXPERIMENTAL

NMR spectra were recorded on a JEOL FX90Q or a Varian GEMINI 300 instrument in $CDCl_3$ solution with tetramethylsilane as a reference. IR spectra were recorded with a Perkin-Elmer M–297 spectrophotometer in KBr plates. Mass spectra were taken on a Varian CH–7 instrument. GC analyses were performed on a Varian Aerograph 1800 and a Varian 3300 gas chromatograph. GC-MS analyses were obtained on Perkin-Elmer Sigma 3 gas chromatograph connected to a Kratos MS–125 spectrometer. UV spectra were recorded on a Pye Unicam SP8–100 UV/VIS spectrophotometer. Column chromatography was performed on silica gel (60–220 nm) using pentane-ether as eluent. A high pressure mercury lamp TQ 150 or 400 W arc was used for irradiation as well as the Rayonet reactor equipped with 350 nm lamps. Irradiations were performed in a Quartz or Pyrex vessel in acetone, benzene or ethanol solutions. All irradiation experiments were carried out in degassed solutions by bubbling a stream of nitrogen prior to irradiation. Solvents were purified by distillation. Melting points were determined on a Thiele apparatus and are uncorrected.

Irradiation of 1 in Acetone

A solution of **1** (162 mg, 1 mmol) in dry acetone (30 ml) was irradiated in a Pyrex tube with a 400 W arc for 3 hours (70% of conversion of **1**). Based on GC–MS analyses (DB–1, 30 m, 200–250 °C), 4 products, ***anti*-8** and ***syn*-8**, and oxetanes ***syn*-9** and ***anti*-9**, were identified in the ratio 7.9 : 3.7 : 2.3 : 1, resp. The products were isolated in 40% yield on silica gel column with pentane-ether (10 to 50%) and described in the order of their elution by chromatography. Stereo isomers are not completely separated despite extensive chromatography. Enriched mixtures in each showed the following *syn*- and *anti*-2′,2′-dimethylspiro[4-oxo-adamantane-2,3′-oxetane] (**9**).

Mixture of not separated stereoisomers. GC–MS: ***syn*-9** *m/z* 220 (M^+, 9%), 190 (22), 161 (76), 133 (24), 118 (33), 104 (33), 91 (100), 76 (32); ***anti*-9** *m/z* 220 (M^+, 8%), 190 (8), 161 (58), 133 (24), 118 (31), 104 (71), 91 (100), 78 (36); ^{1}H NMR δ: 4.40 [(d, 1H, J = 6.3 Hz), ***anti*-9**], 4.21 [(d, 1H, J = 6.3 Hz), ***anti*-9**], 4.05 [(d, 1H, J = 6.5 Hz), ***syn*-9**], 4.03 [(d, 1H, J = 6.5 Hz), ***syn*-9**], 3.12 [(br. s, 1H) ***anti*-9**], 3.06 [(br. s, 1H) ***syn*-9**], 2.52 – 2.40 [(4H), ***syn*-9** and ***anti*-9**],2.21 – 1.62 [(m, 18H) ***syn*-9** and ***anti*-9**], 1.50 [(s, 3H) ***syn*-9**], 1.42 [(s, 3H) ***syn*-9**], 1.37 [(s, 3H) ***anti*-90**], 1.31 [(s, 3H) ***anti*-9**]; ***syn*-9**: ^{13}C NMR δ: 216.17 (s), 88.07 (s), 74.57 (t), 52.83 (s), 51,80 (d), 45.63 (d), 38.30 (t), 35.53 (t), 34.39 (t), 33.27 (t), 31.48 (d), 26.05 (d), 25.50 (q), 25.21 (q).

Anal. Calcd. for $C_{14}H_{20}O_2$ (M_r = 220.30): C 76.32, H 9.15%; found C 76.25, H 9.39%.

anti- and syn-4-(3-Oxobutyl)-2-adamantanones (**8**); ***anti*-8**: ^{1}H NMR δ: 2.58–2.31 (4H, m), 2.13 (3H, s), 2.26– 1.77 (11H, m), 1.56–1.46 (2H, dd, J = 7.5 Hz); ^{13}C NMR:δ: 217.88 (s), 208.42 (s), 51.23 (d), 47.94 (d), 46.75 (d), 40.91 (t), 39.71 (t), 39.52 (t), 37.75 (t), 34.09 (t), 31.43 (d), 29.90 (q), 27.29 (d), 26.61 (t); MS, *m/z* 220 (M^+, 69%), 202 (38) 162 (40), 134 (17), 118 (12), 104 (13), 91 (40), 78 (33), 42 (100); IR ν: 2910 (s), 2850 (s), 1720 (s), 1445 (m), 1415 (w), 1355 (m), 1315 (w), 1235 (m), 1160 (m), 1080 (w), 1060 (m) cm^{-1}.

***syn*-8** (not fully separated from ***anti*-8**): ^{1}H NMR δ: 2.58– 2.31 (4H, m), 2.15 (3H, s), 2.29–1.64 (11H, m), 1.56–1.36 (2H, dd, J = 7.5 Hz); ^{13}C NMR δ: 217.57 (s), 208.42 (s), 50.08 (d), 46.28 (d), 45.14 (d), 41.55 (t), 39.12 (t), 39.09 (t), 32.48 (t), 31.03 (d), 30.17 (t), 30.04 (q), 27.07 (d) 24.57 (t); MS, *m/z* 220 (M^+, 27%), 163 (100), 134 (18), 119 (14), 105 (17), 93 (43), 92 (38) 91 (31), 79 (43).

Anal. Calcd. for $C_{14}H_{20}O_2$ (M_r = 220.30): C 76.32, H 9.15%; found C 76.09, H 9.09%.

*Irradiation of **1** in Benzene*

A solution of **1** (425 mg; 2.6 mmol) in benzene (400 ml) was irradiated in a Pyrex vessel with a 400 W mercury arc for 12 hours (90% of conversion by GC). The solvent was removed under vacuum and the crude product mixture was separated by column chromatography on silica gel with pentane-ether (10 to 50%) as eluent. Based on GC–MS analysis of the crude mixture, 4 components, **11**, **12**, **18** and **19**, were determined in the ratio 4.4 : 1.3 : 1.0 : 1.2, resp. Only **11** was separated (86 mg, 25%) in the first fractions by elution with pentane and its structure determined by comparison of the recorded IR, ^{1}H NMR and MS spectra with the data for 2-methylenenoradamantane.[9] Further elution with pentane-ether (10 to 50%) and ether gave, besides unreacted **1**, a mixture of **18** and **19**. Compound **12**, which was present in the crude reaction mixture, decomposed during separation on the column.

*Irradiation of **1** in Benzene in the Presence of Benzophenone*

To a 20 ml of benzene solution of **1** (135 mg, 0.83 mmol), 170 mg (0.93 mmol) of benzophenone was added and irradiated in a Pyrex tube in a Rayonet reactor equipped with 350 nm lamps for 15 hours (40% of conversion of **1**). After evaporation of solvent, the crude reaction mixture was chromatographed on silica gel column. With pentane-ether (10%) as eluent, a crystalline *syn-2',2'-diphenylspiro[4-oxo-adamantane-2,3'-oxetane]* (***10***) was isolated (87 mg; 75% based on a consumed starting material) and purified by sublimation in vacuum (10 mm Hg, 180 °C) to give a pure compound, m.p. 139–141 °C ^{1}H NMR δ: 7.85–7.72 (4H, m), 7.44–7.18 (6H, m), 4.00 (1H, d, J = 5.6 Hz), 3.98 (1H, d, J = 5.6 Hz), 3.02 (1H, br. s), 2.42 (1H, br. s), 2.32–2.13 (2H, m), 1.98–1.39 (8H, m); ^{13}C NMR δ: 216.23 (s), 142.31 (s), 140.90 (s), 128.21 (d, 2C), 127.87 (d, 2C), 127.33 (d), 127.30 (d), 126.77 (d, 2C), 126.60 (d, 2C), 93.41 (s), 74.33 (t), 57.38 (s), 51.85 (d), 45.74 (d), 38.71 (t), 33.84 (t), 33.62 (t), 32.92 (t), 30.96 (d), 26.07 (d), IR ν: 3060 (w), 2920 (s), 2850 (s), 1715 (s), 1600 (w), 1450 (m), 985 (m), 955 (m), 765 (s), 750 (m), 710 (s) 695 (m) cm^{-1}; MS, *m/z* 344 (M$^+$, 5%), 326 (100), 314 (68), 298 (29), 286 (26), 244 (32), 243 (43), 241 (31), 217 (44), 215 (49), 205 (38), 203 (36), 191 (31), 179 (49), 167 (73), 165 (92), 115 (36), 91 (89), 79 (20).

Anal. Calcd. for $C_{24}H_{24}O_2$ (M_r=344.43): C 83.69, H 7.02%; found: C 83.79, H 7.11%.

*Irradiation of **1** in Ethanol*

A solution of **1** (178 mg, 1.09 mmol) in abs. ethanol (85 ml) was irradiated (TQ–150) in the quartz tube and the reaction was followed by GC (DB 210, 120 °C). After 1.5 hours (85% of conversion of **1**), irradiation was interrupted, the solvent was evaporated and the residue chromatographed on a column packed with basic Al_2O_3 with pentane-ether as eluent. Ketal **13** (26 mg, 10%), starting methylene ketone **1** (62 mg, 35%) and some unidentified tarry material were isolated in a small yield because of its decomposition to **1**.

*4-Methylene-2,2-diethoxyadamantane (**13**):* ^{1}H NMR (C_6D_6) δ: 4.73 (d, 1H, J = 2.3 Hz), 4.67 (d, 1H, J = 2.3 Hz), 3.42 (q, 2H), 3.38 (q, 2H), 2.76 (br. s, 1H), 2.1–1.52 (m, 11H), 1.13 (t, 3H), 1.10 (t, 3H); ^{13}C NMR (C_6D_6) δ: 154.7 (s), 103.9 (t), 102.3 (s), 54.40 (t), 54.17 (t), 45.6 (d), 40.0 (t), 38.6 (d), 36.6 (t), 34.8 (t), 34.1 (t), 33.7 (t), 27.8 (d), 15.68 (q), 15.57 (q); IR ν: 3070 (w), 2980 (w), 2920 (s), 2860 (w), 1445 (w), 1370 (w), 1120 (s), 1055 (s), cm^{-1}; MS, *m/z* 236 (M$^+$, 4%), 192 (30), 165 (100), 91 (14).

*Irradiation of 2-Adamatanone (**20**) in Ethanol*

A solution of **20** (195 mg, 1.3 mmol) in abs. ethanol (100 ml) was irradiated (TQ–150) in a quartz tube for 1.5 hours. The solvent was evaporated and the residue chromatographed on basic Al_2O_3. The product **21** (116 mg) was isolated in 40% yield.

*2,2-Diethoxyadamantane (**21**):* ^{1}H NMR (C_6D_6) δ: 3.38 (q, 4H), 2.12–2.02 (m, 6H), 1.78–1.54 (m, 8H), 1.13 (t, 6H); ^{13}C NMR (C_6D_6) :δ: 101.87 (s), 53.99 (t), 37.84 (t), 34.19 (d and t), 27.75 (d), 15.71 (q); IR ν: 2980 (m), 2920 (s), 2850 (m), 1450 (w), 1380 (w), 1120 (m), 1085 (m), 1055 (m), 1020 (w), cm^{-1}; MS, *m/z* 179 (M$^+$ –OEt, 75%), 151 (40), 67 (100). (HRMS: found: M$^+$ –OEt, 179.140467. Calcd. for $C_{12}H_{19}O$: M–OEt, 179.143041).

*Wolff-Kishner Reduction of syn and anti-4-(3-Oxobutyl)-2-adamantanones (**8**)*

A mixture of *syn* and *anti*-diketones **8** (136 mg, 0.62 mmol), 5 ml diethylene glycol, 210 mg KOH and 0.4 ml hydrazine hydrate was heated for 2 hours at 200 °C and for another 2 hours at 210 °C. Then, the reaction mixture was cooled, diluted with 20 ml of water and extracted with pentane. Pentane extracts were washed with water and dried over anhydrous magnesium sulphate. Filtration and evaporation of solvent afforded 52 mg (44%) of crude 2-(*n*-butyl)adamantane (**14**). An analytical sample was obtained by column chromatography on silica gel using pentane and 5% of ether in pentane as eluent.

2-(n-Butyl)adamantane (**14**): ^{1}H NMR (C_6D_6) δ: 1.82–1.48 (m, 15H), 1.46–1.12 (m, 6H), 0.82 (t, 3H, J = 7.0 Hz); ^{13}C NMR (C_6D_6) δ: 44.31 (d), 39.27 (t, 2C), 38.42 (t), 32.29 (t), 31.83 (d, 2C), 31.58 (t, 2C), 29.85 (t), 28.32 (d), 28.07 (d), 22.95 (t), 14.10 (q); IR ν: 2960 (m), 2910 (s), 2850 (s), 1465 (w), 1450 (w) cm^{-1}; MS, *m/z* 192 (M^+, 25%), 178 (4), 136 (17), 135 (100), 107 (32), 93 (35), 79 (36), 67 (26), 41 (22).

Anal. Calcd. for $C_{14}H_{24}$ (M_r = 192.33): C 87.42, H 12.56%; found C 87.14, H 12.83%.

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SAŽETAK

Fotokemija 4-metilen-2-adamantanona, egzocikličkoga β,γ-nezasićenog ketona

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Proučavane su fotokemijske reakcije 4-metilen-2-adamantanona (**1**) pod uvjetima direktne i fotosenzibilizirane fotolize. Ovisno o primijenjenim uvjetima, β,γ-nezasićeni keton **1** podliježe reakcijama karakterističnima za ketone ili alkene. Izravnim osvjetljavanjem metilen-ketona **1** u benzenu, nastaje smjesa 2-metilennoradamantana (**11**) i 4-metilenbiciklo[3.3.1]non-2-en-7-karbaldehida (**12**). Osvjetljavanjem **1** u benzenu u prisutnosti benzofenona, nastaju oksetani **10**, dok su glavni produkti fotokemijske reakcije u acetonu *syn*- i *anti*-4-(3-oksobutil)-2-adamantanoni (**8**). U protičnom otapalu (etanol), **1** daje isključivo acetal **13**. Premda se na osnovu pojačane $n \rightarrow \pi^*$ apsorpcije u UV spektru metilen-ketona **1** može očekivati reakcija između dva kromofora, produkt oxa-di-π-metano pregrađivanja nije primijećen.