Photocycloaddition of Cyclohex-2-enones to 2-Alkylprop-2-enenitriles

by **Lars Meyer, Bruno Elsholz, Ingo Reulecke, Kerstin Schmidt,** and **Paul Margaretha***

Institut für Organische Chemie, Universität Hamburg, M. L. King Platz 6, D-20146 Hamburg
(Phone: +4940-428384316; fax: +4940-428385592; e-mail: Paul.Margaretha@chemie.uni-hamburg.de)

and **Pablo Wessig**

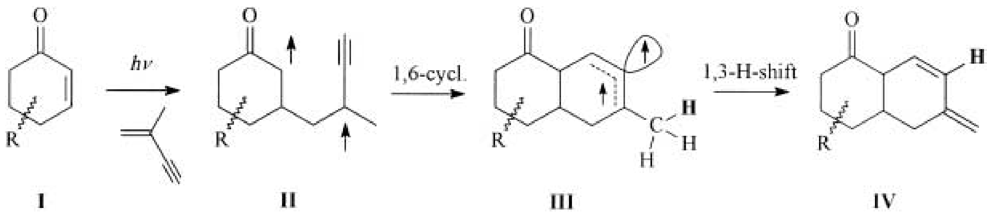
Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, D-12489 Berlin

Dedicated to Professor *Waldemar Adam* on the occasion of his 65th birthday

The outcome of the photocycloaddition of cyclohex-2-enones to 2-alkylprop-2-enenitriles differs basically from that of the corresponding 2-alkylbut-1-en-3-ynes. While the latter afford mainly products resulting from 1,6-cyclization of the intermediate triplet alkyl-(prop-2-ynyl) 1,4-biradical, the former give only cyclobutanecarbonitriles resulting from 1,4-cyclization of the singlet alkyl-cyanoalkyl 1,4-biradical.

Introduction. – We have recently presented results [1][2] on a novel reaction of excited cyclohex-2-enones **I** with 2-methylbut-1-en-3-yne wherein the intermediate triplet biradical **II** undergoes 1,6-cyclization to a (biradicaloid) 1,2-cyclohexadiene **III** and subsequent Me-H-atom transfer to afford methylenenaphthalenones **IV** (*Scheme 1*). We now report that *a*) this intramolecular H-atom transfer can also proceed in an endocyclic mode to give a 1,3-cyclohexadiene instead of a methylenecyclohexene moiety, and *b*) the reaction of cyclohexenones in the presence of the corresponding unsaturated nitriles, *i.e.*, wherein the terminal enyne CH group is formally replaced by a N-atom, afford cyclobutanecarbonitriles selectively to the exclusion of any dihydropyridine derivatives resulting from an analogous 1,6-cyclization.

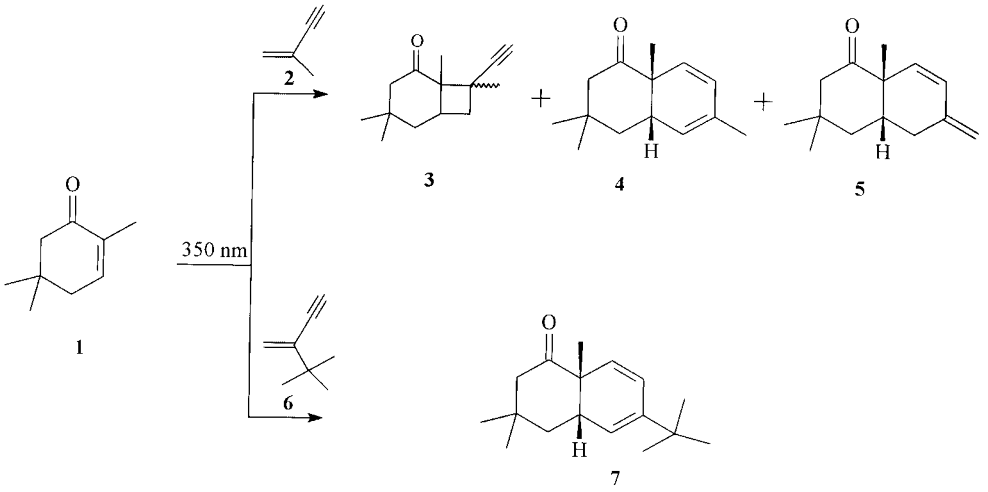
Scheme 1



Results. – Since we had observed [2] that alkyl substituents at both C(2) and C(5) of cyclohex-2-enone favor the formation of naphthalenones, we investigated the photocycloaddition of 2,5,5-trimethylcyclohex-2-enone (**1**) to 2-methylbut-1-en-3-yne (**2**; *Scheme 2*). Irradiation (350 nm) in benzene to *ca.* 67% conversion gives a 19:22:59 mixture of enone and enyne adducts **3**–**5** (increasing retention times, monitored by GC/MS). Isolation of the main fraction by liquid chromatography afforded a 1:2

mixture of naphthalenones **4** and **5**. The observation that apparently the endocyclic H-atom transfer can compete with the exocyclic one led us to explore the photocycloaddition of **1** to 2-(*tert*-butyl)but-1-en-3-yne (**6**). Indeed, irradiation (350 nm) in benzene proceeds smoothly up to 60% conversion to afford enone and enyne adduct **7** selectively (> 75% as monitored by GC/MS). After isolation by liquid chromatography, NMR spectra confirmed the main product **7** to be a naphthalenone with the expected cyclohexa-1,3-diene substructure (*Scheme 2*).

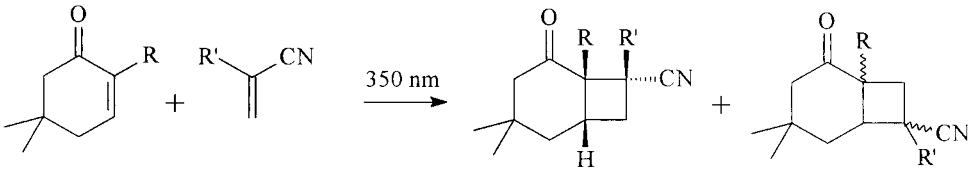
Scheme 2



To extend the scope of the reactions mentioned above to the formation of six-membered aza heterocycles, we next investigated the photocycloaddition of cyclohexenones **1**, **8**, and **9** to the unsaturated nitriles **10** and **11**, respectively. All these reactions can be accomplished to total conversion of the cyclohexenone, in each case with the formation of one major (between 70 and 90%) product, and without any indication of olefinic H-atom signals in the NMR spectra of the crude product mixtures. Indeed, spectroscopic analyses of the main photocycloadducts **12** after purification by liquid chromatography reveals them all to be *endo*-5-oxobicyclo[4.2.0]octane-7-carbonitriles, while the minor products **13** are 2-oxobicyclo[4.2.0]octane-7-carbonitriles with varying configurations (*Scheme 3*).

Discussion. – To find an explanation for the different behavior of acetylenes (**2** and **6**) and nitriles (**10** and **11**) in the ring-closure reactions, we performed DFT calculations (for details *cf. Exper. Part*). These calculations are based on the evidence that cyclization reactions of alkyl-(prop-2-ynyl) biradicals [3] proceed on the triplet potential-energy surface, and that the intersystem crossing occurs subsequently, here in the course of a H shift. Obviously, this does not apply to the 1,4-cyclization to cyclobutanes, which proceeds *via* a singlet-triplet intersection. Two simple model systems, namely the hex-1-yne-3,6-diyl biradical **BR-C** and the 1-cyanobutane-1,4-diyl biradical **BR-N**, which differ in the type of C≡X bond, were chosen (*Scheme 4*). As can

Scheme 3



1 R = Me

8 R = H

9 R = (*t*-Bu)C≡C

10 R' = Me

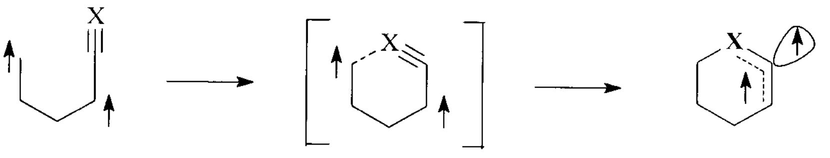
11 R' = *t*-Bu

12

13

a R = R' = Me
b R = Me, R' = *t*-Bu
c R = H, R' = Me
d R = H, R' = *t*-Bu
e R = (*t*-Bu)C≡C, R' = Me
f R = (*t*-Bu)C≡C, R' = *t*-Bu

Scheme 4

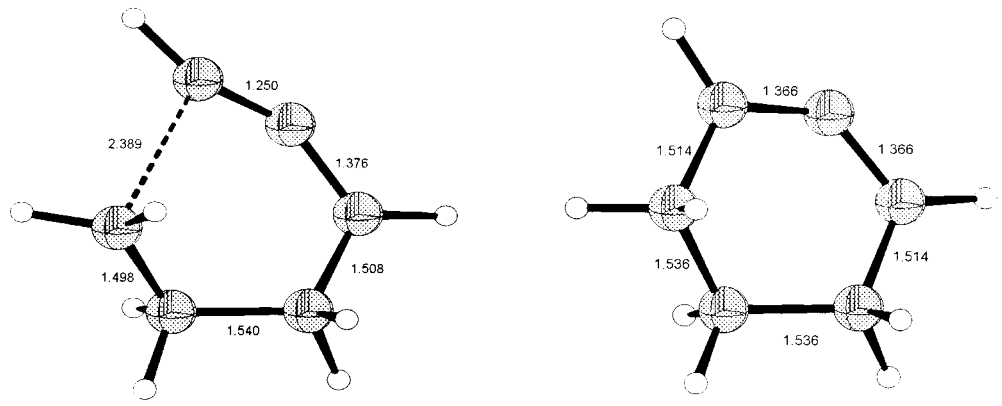


BR **TS** **P**

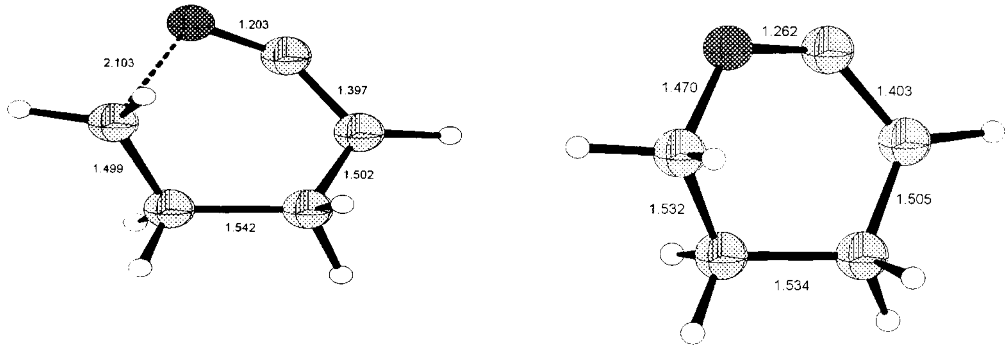
(X = CH, N)

be seen from the values in the *Table*, the 1,6-cyclization (*Scheme 4*) of the acetylene biradical is exothermic, while that of the nitrile biradical is endothermic. This result is understandable, when one looks at the (calculated) structures of both products, **P-CH** and **P-N**, and also compares the two transition states, **TS-CH** and **TS-N**, respectively. As can be seen (*Fig. 1*) the C=N bond in ketenimine **P-N** is remarkably shorter than the corresponding C=C bond in allene **P-CH**, albeit the bond angles are similar in both cases, and, therefore, considerably more strain is built up in the 1,6-cyclization leading to the heterocumulene.

The regio- and stereoselectivity observed in the [2 + 2] photocycloaddition of cyclohexenones to the unsaturated nitriles **10** and **11** is worth mentioning. A preferential formation of so-called *HH* (head to head) regioisomers in the photocycloaddition of cyclohexenones to prop-2-enenitrile has already been observed [4] [5] and discussed [6] by other authors. The formation of *trans*-fused bicyclo[4.2.0]octanecarbonitriles (**13c** and **13d**, *J* (1,6) = 12 Hz) in our reactions is observed only for the *HT* (head to tail) photocycloadducts of cyclohexenone **8**, which bears no substituent at C(2). The differentiation between *cis*- and *trans*-fused bicyclo[4.2.0]octan-2-ones



TS-CH **P-CH**



TS-N **P-N**

Fig. 1. *Calculated structures for transition states and products of the 1,6-cyclization of hex-1-yne-3,6-diyl and 1-cyanobutane-1,4-diyl biradicals*

Table. *Calculated Energy Values for the 1,6-Cyclization of Hex-1-yne-3,6-diyl* (**BR-CH**) *and 1-Cyanobutane-1,4-diyl* (**BR-N**) *Biradicals*

Molecule	E [a])	ZPE [b])	E + ZPE [b])	E_{rel} [b])
BR-CH	– 233.2491969	70.73	– 146295.5	0.00
TS-CH	– 233.2296548	71.53	– 146282.4	+ 13.1
P-CH	– 233.2966019	75.56	– 146320.4	– 24.9
BR-N	– 249.3397258	64.64	– 156398.5	0.00
TS-N	– 249.3095357	65.67	– 156378.6	+ 19.9
P-N	– 249.3417590	68.45	– 156396.0	+ 2.5

[a]) In atomic units. [b]) In kcal/mol.

bearing a bridgehead alkyl group is easily achieved by their ^{1}H-NMR spectra as the geminal coupling constants of the CH_2 group adjacent to the C=O group differ strongly. In the *trans*-fused bicycles, the six-membered ring is only slightly distorted from an ideal chair cyclohexanone ($J \approx -12.5$ Hz); in the *cis*-fused products the ring adopts a twisted-boat conformation, where the C=O group nearly bisects the CH_2 angle, *i.e*, the conformation of maximum hyperconjugation, and therefore the coupling constant decreases to $J \approx -17.5$ Hz [7][8].

The assignment of the *endo*-carbonitrile configuration of the major photocycloadducts **12** results from both from NOESY (nuclear *Overhauser* effect correlation spectroscopy) and from their ^{1}H-NMR spectra, wherein the chemical shifts of the H-atoms *cis* to the *t*-Bu groups are shifted to higher frequencies (*Fig. 2*), an effect that has been already observed for the H-atoms at C(4) in 3,3-dialkylcyclobutenes [9]. The diastereoselectivity observed in the formation of products **12** could be due to attractive charge interactions (either between the C=O C- and the CN N-atom, or the C=O O- and the CN C-atom), which would orient the CN group to the same side of the newly formed cylobutane ring as the adjacent C=O group.

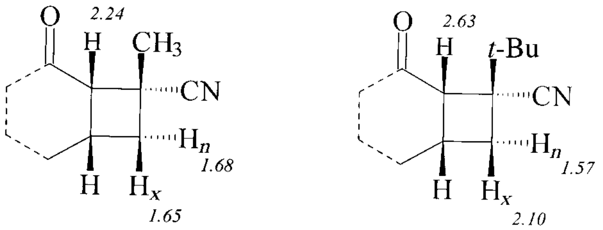


Fig. 2. *Averaged chemical shifts* (in C_6D_6) *of cyclobutane H-atoms of 2-methylprop-2-enenitrile photocycloadducts* **12a**, **12c**, *and* **12e**, *and of 2-(*tert*-butyl)prop-2-enenitrile photocycloadducts* **12b**, **12d**, *and* **12f**, *respectively*

Finally, the concomitant formation of naphthalenones **4** and **5** in the photocycloaddition of **1** to **2** is also noteworthy, as we had not observed any endocyclic H-shift (here leading to **4**) in previous experiments with 2-alkynylcyclohexenones and the same enyne [1][2]. The requirement for a 1,3-H shift to the intermediate trigonal C-atom (*Scheme 5*) is the parallel alignment of the C–H bond at C(1) and the p-orbital at C(3) in intermediate **V**. While, for the formation of naphthalenone **VI** all the three (exocyclic) Me H-atoms fulfill this requirement because of free rotation, for the formation of naphthalenone **VII** one of the ring CH_2 H-atoms must occupy an axial position, which now depends on the conformation adopted by the six-membered ring. Apparently the Me group at C(2) of **1** helps to stabilize the newly formed six-membered ring in a conformation wherein one of the CH_2 H-atoms is, indeed, in an axial position, as reflected by the statistically predicted 1:3 ratio in the formation of endocyclic naphthalenone **4** *vs.* exocyclic naphthalenone **5**. The practical inconvenience of this 1,3-diene formation lies in the fact that such compounds are efficient triplet quenchers, which would explain why reactions such as **1** + **6** → **7** stop at *ca.* 60% conversion.

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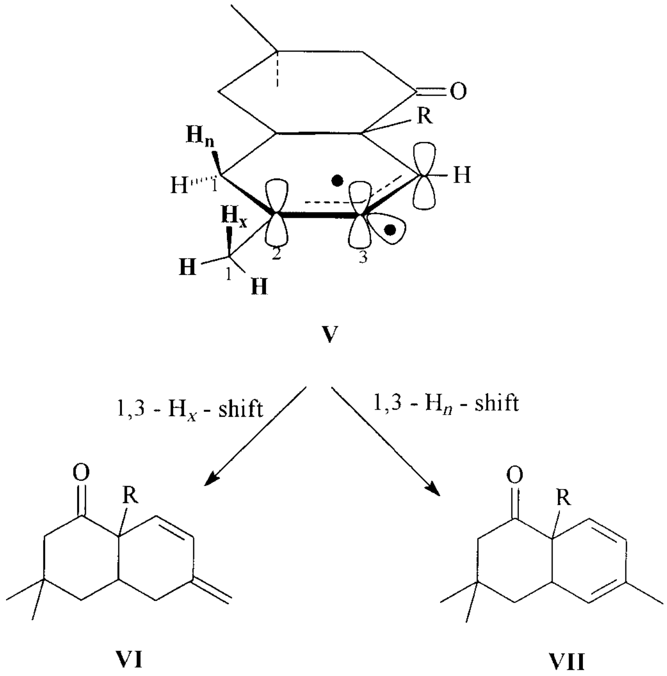
Scheme 5



Experimental Part

1. *General. 2-Methyl prop-2-enenitrile* (**10**) is commercially available. *2-(*tert*-Butyl)prop-2-enenitrile* (**11**) [10], *2-methylbut-1-en-3-yne* (**2**) [11], *2-(*tert*-butyl) but-1-en-3-yne* (**6**) [12], *5,5-dimethylcyclohex-2-enone* (**8**) [13], *2,5,5-trimethylcyclohex-2-enone* (**1**) [14] and *2-(3,3-dimethylbut-1-ynyl)-5,5-dimethylcyclohex-2-enone* (**9**) [15] were prepared according to literature procedures. ^{1}H- and ^{13}C-NMR Spectra: 500 and 125.8 MHz, resp.; chemical shifts δ in ppm rel. to Me_4Si (=0 ppm). EI-MS: 70 eV; in *m/z* (rel. intensity in % of base peak). Photolyses: *Rayonet RPR-100* photoreactor equipped with 350-nm lamps. GC: 30-m *SE-30* cap. column.

2. *Photolyses.* 2.1. *General Procedures.* In the prep. experiments, an Ar-degassed soln. of cyclohexenone (1 mmol), and enyne or unsaturated nitrile (20 mmol) in benzene (10 ml) was irradiated for the time indicated (GC monitoring, peak percentages in increasing retention times), until maximum conversion of the enone was achieved. After evaporation, the residue was worked up by chromatography (CC) on SiO_2.

2.2. *Photolysis of* **1** *and* **2**. Irradiation for 8 h up to 67% conversion of **1** led to three new product peaks (19% (**3**), 22% (**4**), and 59% (**5**)). CC (CH_2Cl_2/pentane 9 : 1) afforded 82 mg (40%) of a 1 : 2 mixture of **4**, **5**, R_f 0.60, as a colorless oil, which was not further separated.

*3,4,4a,8a-Tetrahydro-3,3,6,8a-tetramethyl-2*H*-naphthalen-1-one* (**4**). ^{1}H-NMR (C_6D_6): 5.61 (*dd*, *J* = 1.2, 9.7); 5.26 (*d*, *J* = 9.7); 5.25 (*d*, *J* = 6.0); 2.20 (*d*, *J* = 12.9); 2.15 (*dddd*, *J* = 1.2, 4.4, 6.0, 13.0); 2.07 (*dd*, *J* = 2.5, 12.9); 1.59 (*s*, 3 H); 1.41 (*dd*, *J* = 13.0, 13.2); 1.27 (*s*, 3 H); 1.18 (*ddd*, *J* = 2.5, 4.4, 13.2); 0.70 (*s*, 3 H); 0.67 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 211.7 (*s*); 134.1 (*s*); 126.9 (*d*); 125.6 (*d*); 124.8 (*d*); 52.7 (*t*); 49.0 (*s*); 41.2 (*t*); 40.4 (*d*); 32.1 (*s*); 31.6 (*q*); 24.8 (*q*); 21.2 (*q*); 19.4 (*q*). MS: 204 (44, $M^{+\cdot}$), *120*.

*3,4,4a,5,6,8a-Hexahydro-3,3,8a-trimethyl-6-methylidene-2*H*-naphthalen-1-one* (**5**). ^{1}H-NMR (C_6D_6): 5.98 (*d*, *J* = 10.2); 5.15 (*d*, *J* = 10.2); 4.86 (*s*); 4.82 (*s*); 2.46 (*dd*, *J* = 5.0, 15.2); 2.17 (*d*, *J* = 13.5); 1.96 (*dd*, *J* = 2.7, 13.5); 1.85 (*dd*, *J* = 2.5, 15.2); 1.75 (*dddd*, *J* = 2.5, 4.5, 5.0, 12.7); 1.55 (*dd*, *J* = 12.7, 13.2); 1.26 (*s*, 3 H); 0.93 (*ddd*, *J* = 2.7, 4.5, 13.2); 0.89 (*s*, 3 H); 0.68 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 211.6 (*s*); 140.1 (*s*); 131.4 (*d*); 129.2 (*d*); 115.6 (*t*); 51.9 (*t*); 49.6 (*s*); 41.0 (*t*); 37.9 (*d*); 34.0 (*s*); 32.8 (*t*); 31.7 (*q*); 25.5 (*q*); 22.7 (*q*). MS: 204 (50, $M^{+\cdot}$), *91*.

From the crude reaction mixture: bicyclo[4.2.0]octan-2-one **3**. MS: 204 (3, $M^{+\bullet}$), *82* (also base peak in the MS of **1**).

2.3 *Photolysis of* **1** *and* **6**. Irradiation for 8 h up to 50% conversion of **1** led to four new product peaks (4% (unidentified)), 76% (**7**), and 17% and 3% (both unidentified). CC (CH_2Cl_2/pentane 15:1) afforded 79 mg (33%) of **7**, R_f 0.64, as a light yellow oil.

*6-*tert*-Butyl-3,4,4a,8a-tetrahydro-3,3,8a-trimethyl-2*H*-naphthalen-1-one* (**7**). ^{1}H-NMR (C_6D_6): 5.95 (*dd*, J = 1.5, 9.8); 5.33 (*d*, J = 6.0); 5.31 (*d*, J = 9.8); 2.24 (*d*, J = 13.2); 2.18 (*dddd*, J = 1.5, 4.4, 6.0, 13.0); 2.10 (*dd*, J = 2.6, 13.2); 1.38 (*dd*, J = 13.0, 13.2); 1.26 (*s*, 3 H); 1.17 (*ddd*, J = 2.6, 4.4, 13.2); 1.00 (s, 9 H); 0.72 (*s*, 3 H); 0.71 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 211.9 (*s*); 141.8 (*s*); 129.2 (*d*); 123.8 (*d*); 120.7 (*d*); 52.7 (*t*); 49.0 (*s*); 41.0 (*t*); 40.2 (*d*); 33.6 (s); 32.3 (*s*); 31.7 (*q*); 28.9 (*q*); 24.9 (*q*); 19.2 (*q*). MS: 246 (38, $M^{+\bullet}$), *161*.

2.4 *Photolysis of* **1** *and* **10**. Irradiation for 8 h up to total conversion of **1** led to two new product peaks (73% (**12a**) and 27% (**13a**)). CC (Et_2O/pentane 4:1) afforded first 81 mg (39%) of **12a**, R_f 0.46, and then 27 mg (13%) **13a**, R_f 0.25, both as colorless oils.

*1α,6α-3,3,6,7-Tetramethyl-5-oxobicyclo[4.2.0]octane-7-*endo*-carbonitrile* (**12a**). ^{1}H-NMR (C_6D_6): 2.64 (*d*, J = 17.6); 2.18 (*dd*, J = 2.8, 17.6); 1.81 (*dd*, J = 11.9, 13.6); 1.63 (*m*, 2 H); 1.55 (*dd*, J = 8.2, 11.4); 1.35 (*ddd*, J = 2.8, 7.6, 13.6); 0.92 (*s*, 3 H); 0.89 (*s*, 3 H); 0.71 (*s*, 3 H); 0.48 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 210.6 (*s*); 124.9 (*s*); 53.3 (*t*); 49.7 (*s*); 41.6 (*t*); 36.5 (*d*); 36.1 (*s*); 35.5 (*t*); 32.3 (*s*); 30.9 (*q*); 25.9 (*q*); 20.1 (*q*); 19.4 (*q*). MS: 205 (15, $M^{+\bullet}$), *82*.

1α,6α-1,4,4,7-Tetramethyl-2-oxobicyclo[4.2.0]octane-7-carbonitrile (**13a**). ^{1}H-NMR (C_6D_6): 2.42 (*ddd*, J = 2.8, 8.4, 11.2); 2.04 (*dd*, J = 2.8, 12.6); 1.93 (*dd*, J = 1.9, 17.0); 1.78 (*d*, J = 12.6); 1.72 (*d*, J = 17.0); 1.50 (*s*, 3 H); 0.85 (*m*, 2 H); 0.74 (*s*, 3 H); 0.62 (*s*, 3 H); 0.49 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 214.9 (*s*); 124.2 (*s*); 53.8 (*s*); 51.3 (*t*); 47.2 (*d*); 42.6 (*s*); 41.7 (*t*); 35.6 (*t*); 32.2 (*q*); 29.1 (*s*); 26.7 (*q*); 24.4 (*q*); 20.4 (*q*). MS: 205 (5, $M^{+\bullet}$), *41*.

2.5. *Photolysis of* **1** *and* **11**. Irradiation for 24 h up to 85% conversion of **1** led to two new product peaks (24% (**13b**) and 76% (**12b**)). CC (Et_2O/pentane 2:1) afforded 97 mg (40%) of **12b**, R_f 0.79, as colorless oil.

*1α,6α-7-(*tert*-Butyl)-3,3,6-trimethyl-5-oxobicyclo[4.2.0]octane-7-*endo*-carbonitrile* (**12b**). ^{1}H-NMR (C_6D_6): 2.81 (*d*, J = 18.3); 2.21 (*dd*, J = 2.8, 18.3); 2.05 (*dd*, J = 11.8, 13.4); 2.03 (*dd*, J = 9.1, 12.1); 1.67 (*dddd*, J = 2.2, 7.9, 9.1, 11.8); 1.52 (*dd*, J = 2.2, 12.1); 1.41 (*ddd*, J = 2.8, 7.9, 13.4); 1.13 (*s*, 3 H); 0.95 (s, 9 H); 0.76 (*s*, 3 H); 0.52 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 210.8 (*s*); 125.3 (*s*); 53.1 (*t*); 49.5 (*s*); 41.4 (*t*); 36.3 (*s*); 36.2 (*d*); 33.1 (*s*); 31.3 (*q*); 30.8 (*t*); 26.9 (*q*); 26.2 (*q*); 24.9 (*s*); 22.6 (*q*). MS: 247 (0.1, $M^{+\bullet}$), *41*.

*1α,6α-7-(*tert*-Butyl)-1,4,4-trimethyl-2-oxobicyclo[4.2.0]octane-7-carbonitrile* (**13b**). MS: 247 (0.7, $M^{+\bullet}$), *41* (from the crude mixture).

2.6. *Photolysis of* **8** *and* **10**. Irradiation for 8 h up to total conversion of **8** led to three new product peaks (75% (**12c**), 9% (unidentified) and 16% (**13c**)). CC (Et_2O/pentane 1:1) afforded 102 mg (53%) of **12c**, R_f 0.53, as a colorless oil.

*1α,6α-3,3,7-Trimethyl-5-oxobicyclo[4.2.0]octane-7-*endo*-carbonitrile* (**12c**). ^{1}H-NMR (C_6D_6): 2.48 (*d*, J = 17.4); 2.28 (*d*, J = 8.5); 2.10 (*dd*, J = 2.8, 17.4); 1.88 (*ddddd*, J = 2.5, 8.0, 8.5, 8.5, 11.3); 1.68 (*dd*, J = 2.5, 12.3); 1.63 (*dd*, J = 11.3, 13.6); 1.50 (*dd*, J = 8.5, 12.3); 1.29 (*ddd*, J = 2.8, 8.0, 13.6); 1.04 (*s*, 3 H); 0.70 (*s*, 3 H); 0.46 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 207.8 (*s*); 123.7 (*s*); 53.4 (*t*); 52.8 (*d*); 41.1 (*t*); 37.5 (*t*); 34.7 (*s*); 32.9 (*s*); 28.1 (*q*); 27.8 (*d*); 26.6 (*q*); 25.5 (*q*). MS: 191 (42, $M^{+\bullet}$), *83*.

1α,6β-4,4,7-Trimethyl-2-oxobicyclo[4.2.0]octane-7-carbonitrile (**13c**). MS: 191 (33, $M^{+\bullet}$), *68* (from the crude mixture).

2.7. *Photolysis of* **8** *and* **11**. Irradiation for 24 h up to total conversion of **8** led to two new product peaks (29% (**13d**) and 71% (**12d**)). CC (pentane/Et_2O 6:1) afforded first 116 mg (49%) of **12d**, R_f 0.27, and then 27 mg (13%) of **13d**, R_f 0.12, both as colorless oils.

*1α,6α-7-(*tert*-Butyl)-3,3-dimethyl-5-oxobicyclo[4.2.0]octane-7-*endo*-carbonitrile* (**12d**). ^{1}H-NMR (C_6D_6): 2.70 (*d*, J = 8.5); 2.57 (*d*, J = 16.7); 2.16 (*dd*, J = 2.8, 16.7); 1.90 (*m*, 2 H); 1.75 (*dd*, J = 11.3, 13.5); 1.53 (*dd*, J = 1.8, 12.3); 1.37 (*ddd*, J = 2.8, 7.2, 13.6); 0.84 (*s*, 9 H); 0.73 (*s*, 3 H); 0.68 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 208.1 (*s*); 123.4 (*s*); 53.9 (*t*); 45.4 (*d*); 41.7 (*t*); 33.5 (*s*); 33.1 (*t*); 31.6 (*q*); 29.6 (*t*); 27.9 (*s*); 27.1 (*d*); 25.8 (*q*); 24.9 (*q*). MS: 233 (10, $M^{+\bullet}$), *121*.

*1α,6β-7-(*tert*-Butyl)-4,4-dimethyl-2-oxobicyclo[4.2.0]octane-7-carbonitrile* (**13d**). ^{1}H-NMR (C_6D_6): 2.60 (*ddd*, J = 6.0, 10.7, 12.6); 2.09 (*ddd*, J = 3.1, 12.6, 12.6); 2.05 (*dd*, J = 10.7, 10.9); 1.77 (*dd*, J = 6.0, 11.0); 1.76, 1.72 (*AB*, J = 13.8, 2 H); 1.63 (*dd*, J = 12.6, 12.6); 1.15 (*dd*, J = 3.1, 12.6); 0.84 (*s*, 9 H); 0.72 (*s*, 3 H); 0.68 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 203.1 (*s*); 121.0 (*s*); 54.4 (*t*); 47.1 (*d*); 46.4 (*d*); 42.2 (*t*); 35.1 (*s*); 33.6 (*s*); 31.9 (*q*); 29.6 (*t*); 27.9 (*s*); 25.8 (*s*); 24.7 (*q*). MS: 233 (22, $M^{+\bullet}$), *68*.

2.8. *Photolysis of* **9** *and* **10**. Irradiation for 8 h up to 90% conversion of **9** led to one new product peak (**12e**). CC (pentane/EtOAc 6:1) afforded first 189 mg (70%) of **12e**, R_f 0.63, as a light yellow oil and then 6 mg of **9**, R_f 0.41.

*1α,6α-6-(3,3-Dimethylbut-1-ynyl)-3,3,7-trimethyl-5-oxobicyclo[4.2.0]octane-7-*endo*-carbonitrile* (**12e**). ^{1}H-NMR (C_6D_6): 2.45 (*d*, *J* = 17.8); 2.38 (*dddd*, *J* = 3.6, 8.1, 8.6, 11.2); 2.28 (*dd*, *J* = 2.6, 17.8); 1.89 (*dd*, *J* = 8.6, 12.2); 1.73 (*dd*, *J* = 3.6, 12.2); 1.58 (*dd*, *J* = 11.2, 13.8); 1.39 (s, 3 H); 1.35 (*ddd*, *J* = 2.6, 8.1, 13.8); 1.10 (*s*, 9 H); 0.72 (*s*, 3 H); 0.66 (*s*, 3 H). ^{13}C-NMR (C_6D_6): 204.4 (*s*); 123.7 (*s*); 96.4 (*s*); 77.1 (*s*); 52.4 (*t*); 51.0 (*s*); 40.9 (*t*); 38.7 (*d*); 36.9 (*s*); 36.5 (*t*); 32.6 (*s*); 31.0 (*s*); 30.2 (*q*); 27.8 (*s*); 26.5 (*q*); 23.4 (*q*). MS: 271 (1, $M^{+\bullet}$), *148*.

2.9. *Photolysis of* **9** *and* **11**. Irradiation for 24 h up to 80 % conversion (*monitoring by* ^{1}*H-NMR*). CC (pentane/Et_2O 3 : 1) afforded first 190 mg (60%) of **12f**, R_f 0.66, as colorless crystals, m.p. 73 – 75°, and then 7 mg of **9**, R_f 0.36.

*1α,6α-7-(*tert*-Butyl)-6-(3,3-dimethylbut-1-ynyl)-3,3-dimethyl-5-oxobicyclo[4.2.0]octane-7-*endo*-carbonitrile* (**12f**). ^{1}H-NMR (C_6D_6): 2.49 (*d*, *J* = 18.0); 2.47 (*dddd*, *J* = 4.1, 7.9, 9.8, 11.1); 2.35 (*dd*, *J* = 9.8, 12.3); 2.34 (*dd*, *J* = 2.5, 18.0); 1.64 (*dd*, *J* = 11.1, 13.9); 1.63 (*dd*, *J* = 4.1, 12.3); 1.42 (*ddd*, *J* = 2.6, 7.9, 13.9); 1.28 (*s*, 3 H); 1.25 (*s*, 9 H); 1.17 (*s*, 3 H); 1.07 (*s*, 9 H). ^{13}C-NMR (C_6D_6): 205.1 (*s*); 123.8 (*s*); 96.7 (*s*); 79.9 (*s*); 52.3 (*t*); 50.4 (*s*); 41.8 (*t*); 38.9 (*d*); 36.0 (*s*); 32.3 (*s*); 31.4 (*t*); 31.3 (*q*); 31.0 (*q*); 30.7 (*q*); 30.5 (*s*); 27.1 (*s*); 26.5 (*q*). MS: 313 (3, $M^{+\bullet}$), *148*.

3. *Quantum-Chemical Calculations.* The geometry optimizations were performed with the program package Gaussian 98, Revision A.9 [16] and the B3PW91 (*Becke*'s 3) hybrid functional [17] with the nonlocal correlation provided by the Perdew 91 expression [18] and the 6-31G* basis set. At this same level of theory, frequency calculations were carried out to characterize each structure as either a minimum (**BR**, **P**) or transition state (**TS**), and to obtain the zero-point vibrational energies. Afterwards, single-point calculations were performed with the same DFT functional with the extended 6-311 + + G** basis set in order to obtain improved energies.

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