Revue Roumaine de Chimie, **2009**, *54*(11-12), 895–902

Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)

6,6-DIMETHYL- AND 6,6-DIPHENYLFULVENE AS CYCLOADDENTS IN REACTION WITH MOORE'S KETENE*

Luminitza PÂRVULESCU,[a,**] Anca MARTON,[a] Marina MIHAI,[b] Constantin DRĂGHICI,[b] Richard A. VARGA[c] and Mircea D. GHEORGHIU[d, e, **]

[a] Faculty of Applied Chemistry and Materials Science, "Politehnica" University of Bucharest, Splaiul Independentei 313, 060042 Bucharest, Roumania
[b] "C. D. Nenitzescu" Institute of Organic Chemistry, Roumanian Academy, Splaiul Independentei 202B, 060023 Bucharest, Roumania
[c] Chemistry Department, Babes-Bolyai University, Cluj-Napoca, Arany Janos Str. no. 11, RO-400028 Cluj, Roumania
[d] Department of Chemistry, Massachusetts Institute of Technology, Massachusetts Av. 77, Cambridge, MA 02139, USA
[e] Mount IDA College, Newton, MA 02459, USA

Received June 9, 2009

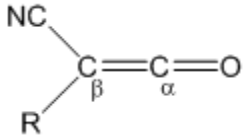
The cycloaddition reactions of *t*-butylcyanoketene (TBCK, Moore's ketene) with 6,6-dimethylfulvene and 6,6-diphenylfulvene produce only the cyclobutanones 6-tert-butyl-7-oxo-2-(propan-2-ylidene)bicyclo[3.2.0]hept-3-ene-6-carbonitrile and 6-tert-butyl-7-oxo-2-(diphenylmethylene)bicyclo[3.2.0]hept-3-ene-6-carbonitrile, respectively. The X-ray diffraction study of the resulted cyclobutanones illustrates that the CO group is in the vicinity of the exocyclic fulvenic double bond and the *cyano* group is in *cis* relationship with the fulvene moiety. By the correlation of the ^{1}H and ^{13}C NMR spectral data of the two cyclobutanones, a similar structure was assigned for the cyclobutanone resulted in the TBCK addition to the 6,6-dimethylfulvene.

INTRODUCTION

For many years the cycloaddition reactions of fulvenes to ketenes[1] have been a subject of interest, both from a theoretical and from a practical point of view. Such reactions have multiple applications in the syntheses of biological active compounds (ophiobolin, prostaglandin precursors,[2] β-lactam antibiotic analogues,[3] pyrethroids[4]). Several fulvenes and ketenes were approached in this context. The most frequently studied were the symmetrical ketenes, which, on this base, offer less information upon the stereospecificity of the cycloadditions: dichloroketene,[2,4-9] dimethylketene,[10-12] diphenylketene.[11-13]

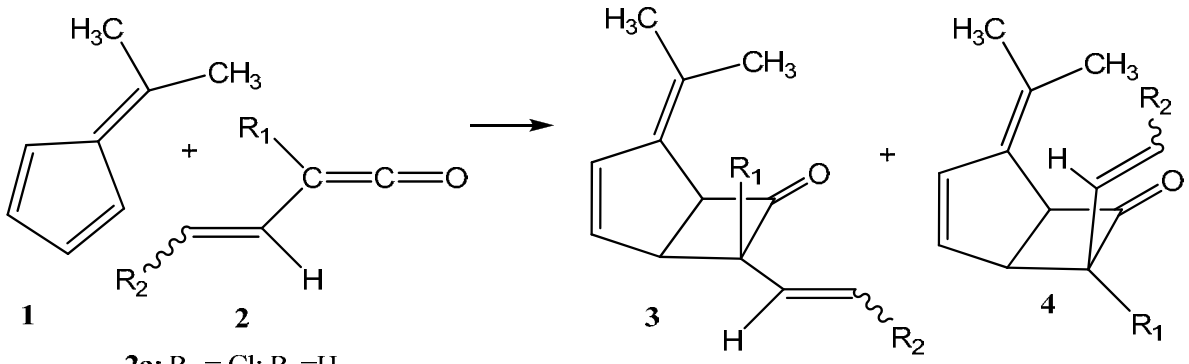
The only examples of fulvenes cycloadditions to unsymmetrical ketenes are illustrated with vinylketenes[14] (Scheme 1) and acylketene[15] (Scheme 2).

We report here our findings concerning the cycloaddition of Moore's ketene (TBCK) which is relatively a highly electrophilic ketene to the enhanced nucleophilic ketenophiles such as dimethyl- and diphenylfulvenes. The enhancement of the electrophilicity of the C_α carbon atom in cyanoketenes is attributed to the presence of the CN group in the molecule.[16]



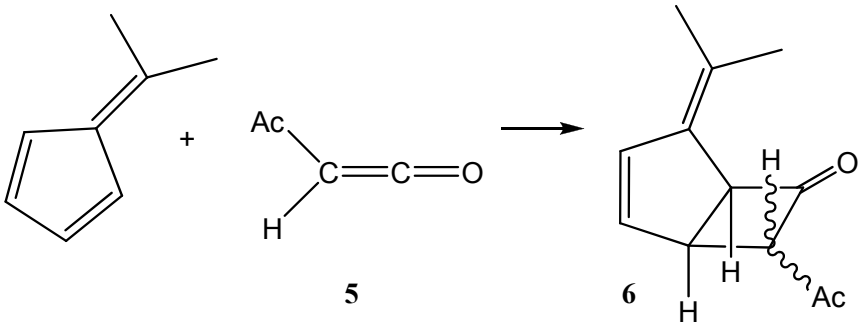
* Presented in part at 2nd EuCheMS Chemistry Congress, Torino, September 16-20, 2008, I.O-S/P-085 and CHIMIA 2009-NEW TRENDS IN APPLIED CHEMISTRY, Constantza, Roumania, May 13-16, 2009, Book of Abstracts p. 67, PA15.

** Corresponding authors: mircea@mit.edu; lr_parvulescu@chim.upb.ro



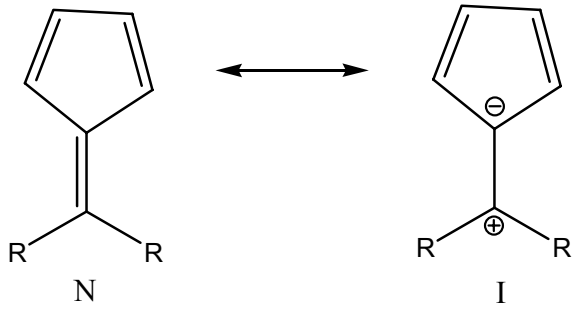
2a: R_1 = Cl; R_2=H
2b: R_1 = CH_3; R_2=H
2c: R_1 = Cl; R_2=C_2H_5

Scheme 1



Scheme 2

On the other hand, the reactivity of five membered ring of fulvene is enhanced because it is electron rich, as a result of the participation of the polar resonance structure **I**. The actual amount of the negative electron density within the five membered ring can be tuned by the substituents R. Any R group with stabilizing ability of the adjacent carbocation will increase the weight of the ionic resonance structure **I**. Indeed, computationally (at B3LYP/6-311++G(d,p) level[17a] and by the way of the Natural Resonance Theory[17b], the following estimates for the weight of the ionic resonance structure (provided using NBO5 package[17c]) resulted: **I**(H): 15%; **I**(Me): 23%; and, **I**(CH=CH): 39%. Also, intuitively, for the diphenylfulvene one expects a high participation of the ionic resonance structure.



1. R = H; 2. R= Me; 3. R,R : CH=CH

N stands for neutral; I stands for ionic

We have chosen to examine the cycloaddition of a very electrophilic ketene to a highly nucleophilic ketenophile. Therefore, one might anticipate a stepwise reaction of ketene cycloaddition rather than a synchronous [2+2] cycloadition. After the electrophilic attack of the carbon from the CO group in the ionic intermediate, both the positive and the negative charges are highly stabilized by resonance. The stepwise cycloaddition produces the cyclobutanone with an ***exo*** configuration of the bulky t-Bu group, similarly to our previous findings when *p*-methoxystyrene[18a] and vinylferrocene[18b] have been used as ketenophiles with TBCK.

In principle, ketene may add to the five membered ring, reaction which is HOMO controlled, and/or to the exocyclic double bond, reaction that is HOMO-1 controlled (see Figure 1):

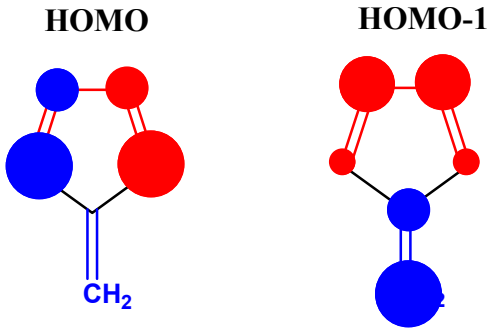
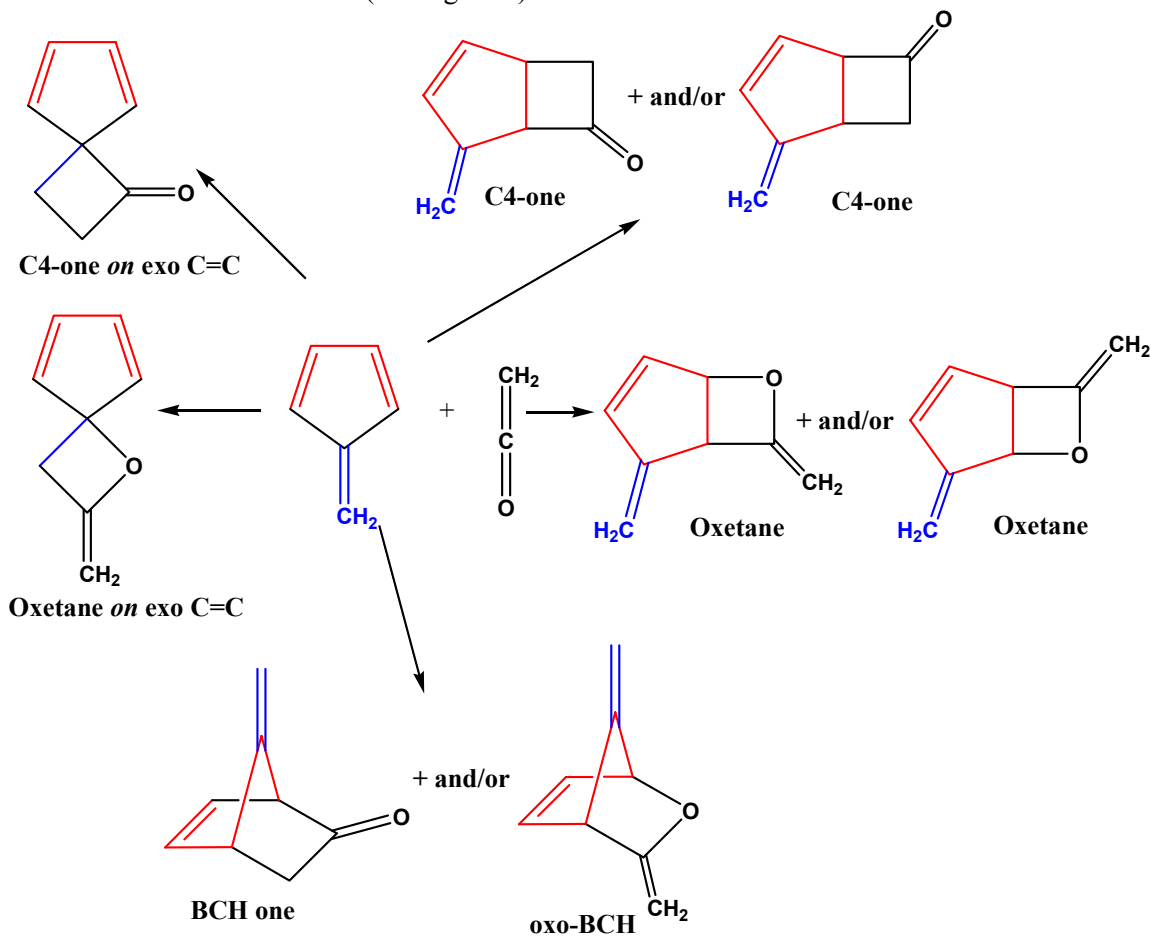


Fig. 1 – HOMO and HOMO-1 of fulvene (computed[19] at B3LYP/6-31G+ level).

Cycloadditon to the five membered ring could occur either as a [2+2] process yielding cyclobutanones (abbreviated as **C4-one**) and/or oxetanes, or as a [4+2] Diels-Alder cycloaddition, affording bicycloheptane products (abbreviated as **BCH**):



Scheme 3

Cycloaddition to the exocyclic C=C bond could provide cyclobutanone(s) and/or oxetane. To our best knowledge, the cyclobutanone attached to the five-membered ring is the only product formed from ketenes and fulvenes. No cycloaddition of ketene to the exo double bond has been documented so far.

We also present the X-ray diffraction results that prove the structure of the cyclobutanone resulted from cycloaddition of TBCK to 6,6-

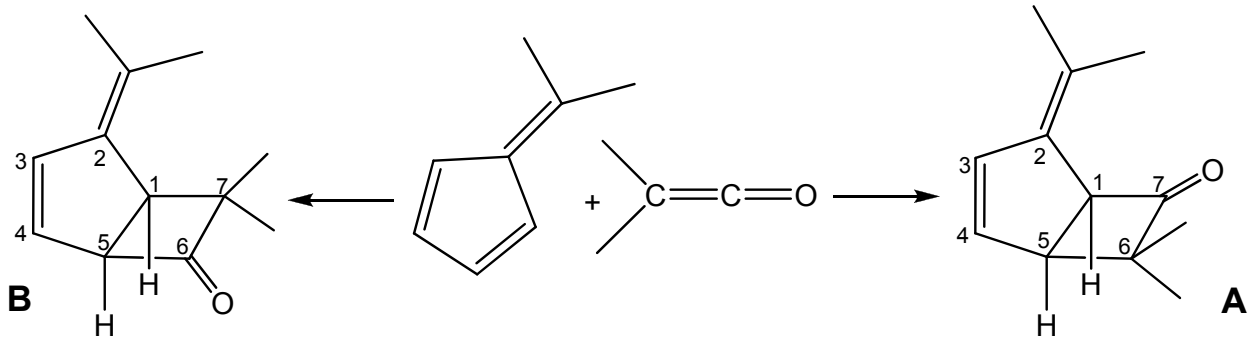
diphenylfulvene. The proven stereochemistry of this adduct is also confirming the structure we have advanced, based on the ^{1}H and ^{13}C-NMR data.[20,21]

RESULTS AND DISCUSSION

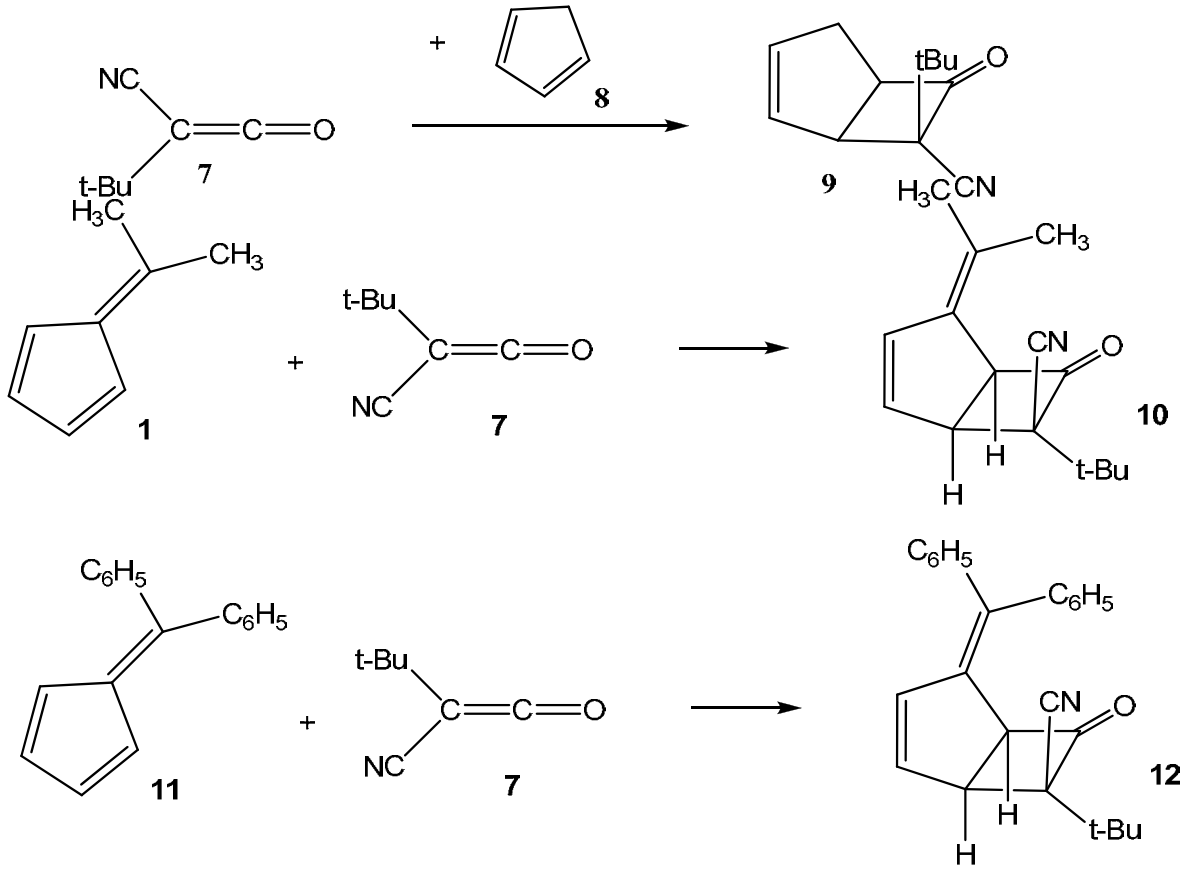
Frontier molecular orbitals analysis concerning the regiospecificity of ketene cycloaddition to fulvene[22,23] is preferentially predicting the formation of a cyclobutanone of "**A**" type:

Indeed, the cycloadditions that we have performed using 6,6-dimethylfulvene **1**, and 6,6-diphenylfulvene **11** and TBCK afforded as only products the cyclobutanones **10** and **12** respectively.

The cycloaddition is regio- and stereospecific. The regiospecificity is similar to the cycloaddition of TBCK to cyclopentadiene,[24] however the stereospecificity differs (see Scheme 5).



Scheme 4



Scheme 5

The structure assignment for the two cyclobutanones **10** and **12**, presenting a *trans* relationship of the *t*-Bu group and the fulvene moiety was done based on spectral information provided by ^{1}H and ^{13}C-NMR data, obtained with or without NMR shift reagents. The collected spectral data were compared to those concerning cyclobutanone models of I and II type (Figure 2):

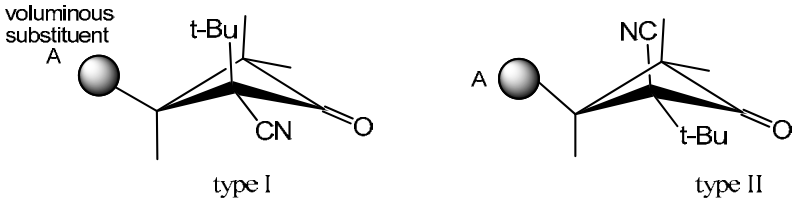


Fig. 2.

In cyclobutanones of type I (A is C_6H_5, p-C_6H_4—C_6H_5, 1-naphtyl or 2-naphtyl) the voluminous groups, A and t-Bu, are *vicinal* and *cis* related. In models of type II (A is ferrocenyl, anthryl, p-CH_3O—C_6H_4, Cl) these groups are *trans* related.[21,25,26] For both types I and II, structures have been confirmed by X-ray diffractometry.[18, 27,28]

For both cycloadducts **10** and **12** and type II cyclobutanones, the chemical shifts for the t-Bu group are greater than 1.1 ppm (while the same shifts in the type I cyclobutanones are less than 1.1 ppm). A second outstanding argument for the structure assignment is provided by the ^{13}C-NMR chemical shift of the CN group: values of 115.55 ppm and 115.71 ppm in compounds **10** and **12** respectively confirm the shielding of this group induced by the *cis* related fulvene moiety (in type I models the analogue chemical shifts show values of 119 ppm).

X-ray data for the cyclobutanone obtained from TBCK and diphenylfulvene provide two prominent information. The first is the confirmation that the regioisomer cyclobutanone is indeed the compound 12. Secondly, the configuration of the t-Bu group is *exo*, e,g. opposite to the five membered ring. Thus, the steric repulsion is diminished, mirrored in the relative short C_{17}-C_{20} bond distance of 1.589 Å, similar to the data acquired from the X-ray of the cyclobutanone obtained from TBCK and p-methoxystyrene.[18a] If the *t*-Bu group is *endo* (or cis) to the bulky group of ketenophile, the same bond distance is elongated and becomes more than 1.6 Å,[18a,29] as a result of the energetical trading to diminish the steric repulsion among the vicinal bulky groups originating from the ketene and the ketenophile.

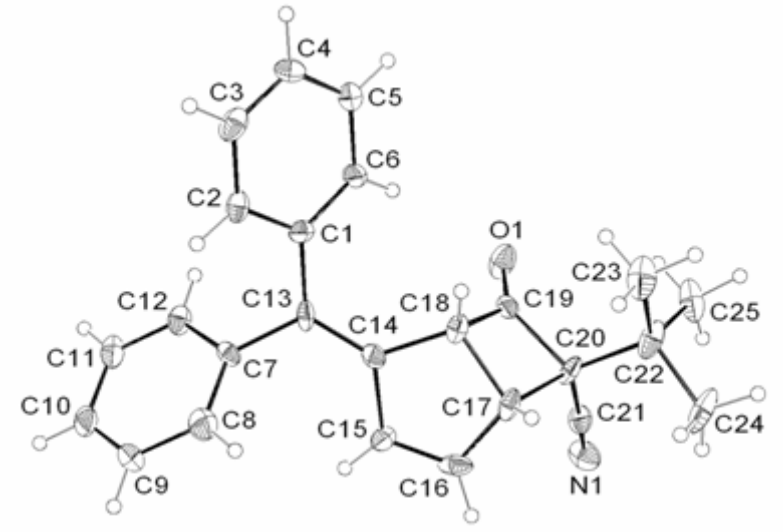


Fig. 3 – ORTEP representation of cyclobutanone **12.**

EXPERIMENTAL

Anhydrous benzene (CHIMOPAR, S.A., Bucharest) was dried over sodium wire. The 2,5-diazido-3,6-di-t-butyl-1,4-benzoquinone has been synthesized starting from 2,5-di-*t*-butylhydroquinone according to the protocol developed by us.[30] The NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer.

6-tert-Butyl-7-oxo-2-(propan-2-ylidene)bicyclo[3.2.0]hept-3-ene-6-carbonitrile (**10**).

t-Butylcyanoketene was generated *in situ* by thermolysis of 2,5-diazido-3,6-di-t-butyl-1,4-benzoquinone in anhydrous benzene.[31] 2,5-Diazido-3,6-di-*t*-butyl-1,4-benzoquinone (3.0 g; 9.9 mmol) was decomposed in 50 mL anhydrous benzene at reflux temperature. A solution of 0.8 g (7.5 mmol) of 6,6-dimethylfulvene in 10 mL of anhydrous benzene was dropwise added and followed by additional reflux for 11 hours. The solvent was removed and the crude reaction mixture was chromatographed on silica (Merck, Si 60) with carbon tetrachloride. A second fraction was re-chromatographed on silica with carbon tetrachloride to yield 0.5g (30%) of pure cyclobutanone **10** as a pale yellow oil (calculated for $C_{15}H_{19}ON$: C, 78.60; H, 8.29 ; N, 6.11. Found: C, 78.61; H, 8.6; N, 6.15%).

^{1}H-NMR [$CDCl_3$, δ (ppm), J (Hz)]: 1.17 (s, 9H, t-Bu); 1.84 (s, 6H, two Me); 3.41 (m, 1H, H^5); 4.41 (m, 1H, H^1); 6.05 (m, 1H, H^4); 6.64 (dd, 5.6, 1.4; 1H, H^3). ^{13}C-NMR [($CDCl_3$, δ (ppm),]: 21.05 (CH_3); 22.30 (CH_3); 25.83 (CH_3-*t*-Bu); 35.67 (Cq-tBu); 42.81(C_5); 66.05(C_1); 73.91(C_6); 115.85 (C≡N); 129.08 (C_2); 131.15 (C_4); 134.16 (C_8); 135.83 (C_3); 198.33 (C_7).

6-tert-Butyl-7-oxo-2-(diphenylmethylene)bicyclo[3.2.0]hept-3-ene-6-carbonitrile (**12**).

2.0 g (6.6 mmol) of 2,5-Diazido-3,6-di-*t*-butyl-1,4-benzoquinone were decomposed in 50 mL anhydrous benzene at reflux temperature. A solution of 1.1 g (4.78 mmol) of 6,6-diphenylfulvene[32] in 15 mL of anhydrous benzene was dropwise added and followed by 10 hours of additional reflux. The solvent was evaporated and the solid residue was chromatographed on silica (Merck, Si 60) with carbon tetrachloride, yielding 0.7g (42%) of pure cyclobutanone **12** (calculated for $C_{25}H_{23}ON$: C, 84.98; H, 6.51 ; N, 3.96. Found: C, 84.99; H, 6.59; N, 3.99%).

^{1}H-NMR [$CDCl_3$, δ (ppm), J (Hz)]: 1.17 (s, 9H, t-Bu); 3.76 (ddd, 6.7, 2.7, 7.1,1H, H^5); 4.44 (dd, 6.7, 1.0, 1H, H^1); 6.22 (ddd, 5.6, 1.4, 2.7, 1H, H^4); 6.57 (dd, 5.6, 1.4; 1H, H^3); 7.16 (dd, 7.4, 1.2, 2H, H_{ortho} first phenyl); 7.30-7.42 (m, 6H $_{meta+para}$); 7.46 (dd 8.0, 1.8, 2H, H_{ortho} second phenyl). ^{13}C-NMR [($CDCl_3$, δ (ppm),]: 26.13 (CH_3-*t*-Bu); 35.88 (Cq-tBu); 44.08 (C_3); 68.24 (C_1); 73.64 (C_6); 115.71 (C≡N); 127.52 (CH); 127.7 (CH); 128.14 (CH); 129.39 (CH); 130.12 (CH); 133.97 (CH); 138.40 (C_3); 141.01(C_9); 141.39(C_9); 198.84(C_7).

X-ray Diffraction Studies. Data collection and processing were carried out using a Bruker AXS SMART APEX system ("Babes-Bolyai" University, Cluj, Romania). Crystal of dimensions 0.24 x 0.23 x 0.02 mm, was mounted on a cryo loop and optically centered**.** The data were collected on a Bruker AXS three-circle platform goniometer equipped with a CCD area detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å at 297(2) K). The structure was solved by direct methods SHELXS-97[33] and successive difference Fourier syntheses and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[33] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed at idealized positions with isotropic thermal parameters set at 1.5 times for the methyl hydrogens and 1.2 for the rest, respectively, of the carbon atom to which they were attached. The methyl groups were allowed to rotate but not to tip. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography.[34] The drawing was created with the ORTEP[35] program.

Table 1

Crystal data and structure refinement

Empirical formula	C25 H23 N O
Formula weight	353.44
Temperature	297(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 9.8760(15) A alpha = 90 deg. b = 7.0847(11) A beta = 93.783(3) deg. c = 28.373(5) A gamma = 90 deg.
Volume	1980.9(5) A^3
Z, Calculated density	4,1.185 Mg/m^3
Absorption coefficient	0.071 mm^-1
F(000)	752
Crystal size	0.24 x 0.23 x 0.02 mm
Theta range for data collection	1.44 to 25.00 deg.
Limiting indices	-11<=h<=11, -8<=k<=8, -33<=l<=33
Reflections collected / unique	18193 / 3499 [R(int) = 0.1865]
Completeness to theta = 25.00	100.0 %
Max. and min. transmission	0.9987 and 0.9831
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3499 / 0 / 248
Goodness-of-fit on F^2	1.154
Final R indices [I>2sigma(I)]	R1 = 0.1645, wR2 = 0.2933
R indices (all data)	R1 = 0.2459, wR2 = 0.3335
Extinction coefficient	0.0021(14)
Largest diff. peak and hole	0.316 and -0.328 e.A^-3

Table 2

Selected bond lengths [Å] and angles [deg]

Bond lengths		Bond angles	
C(13)-C(14)	1.346(10)	C(14)-C(13)-C(1)	122.9(7)
C(14)-C(15)	1.476(11)	C(14)-C(13)-C(7)	121.1(7)
C(14)-C(18)	1.528(11)	C(13)-C(14)-C(15)	127.4(7)
C(15)-C(16)	1.329(11)	C(13)-C(14)-C(18)	127.6(7)
C(16)-C(17)	1.497(12)	C(15)-C(14)-C(18)	104.6(7)
C(17)-C(18)	1.548(10)	C(16)-C(15)-C(14)	111.4(8)
C(17)-C(20)	1.568(10)	C(15)-C(16)-C(17)	113.6(7)
C(18)-C(19)	1.541(11)	C(16)-C(17)-C(18)	102.0(7)
C(19)-O(1)	1.178(9)	C(16)-C(17)-C(20)	114.7(7)
C(19)-C(20)	1.568(11)	C(18)-C(17)-C(20)	92.3(6)
C(20)-C(21)	1.465(12)	C(14)-C(18)-C(19)	115.2(7)
C(20)-C(22)	1.560(12)	C(14)-C(18)-C(17)	106.7(7)
C(21)-N(1)	1.140(10)	C(19)-C(18)-C(17)	87.1(6)
		O(1)-C(19)-C(18)	134.7(8)
		O(1)-C(19)-C(20)	132.7(7)
		C(18)-C(19)-C(20)	92.6(6)
		C(21)-C(20)-C(22)	112.0(6)
		C(21)-C(20)-C(19)	111.7(7)
		C(22)-C(20)-C(19)	115.2(7)
		C(21)-C(20)-C(17)	113.0(7)
		C(19)-C(20)-C(17)	85.4(5)
		N(1)-C(21)-C(20)	177.4(9)
		C(23)-C(22)-C(24)	110.4(8)
		C(23)-C(22)-C(25)	109.1(8)
		C(24)-C(22)-C(25)	109.2(7)

CONCLUSIONS

Cyclobutanone is the only product resulted in the cycloaddition of TBCK to dimethyl- and diphenylfulvenes. The TBCK cycloaddition to the mentioned fulvenes is regiospecific and stereoselective. TBCK adds to fulvene endocyclic C=C double bond to yield the cyclobutanones **10** and **12**, respectively. In both cyclobutanones the bulky *t*-Bu group has *exo* configuration. The structure assignments of cyclobutanones resulted from analytical methods based on ^{1}H- and ^{13}C-NMR and the single-crystal X-ray diffraction study. The stereochemistry of both cyclobutanones confirm and expand our previous results and the correlation between the chemical shifts values and the steric relationship between the voluminous substituents of these cyclobutanones.

Furthermore, relating the geometry of the adducts to the reaction mechanism, in the case of the cycloaddition of TBCK to the above mentioned fulvenes, we hypothesize a non synchronous reaction pathway.

Acknowledgements. LP, AM and CD thank the Roumanian Ministry of Education and Science (grant number CNCSIS CH380803) for the generous financial support. MDG is grateful for support to Chemistry Department, MIT.

REFERENCES

1. T. T. Tidwell, Ketenes, 2nd Ed, Wiley-Interscience, Hoboken, N.J., 2006
2. (a) L. A. Paquette, J. A. Colapret and D. R. Andrews, *J. Org. Chem*., **1985**, *50*, 201-205; (b) G. A. Tolstikov, M. S. Miftakhov, R. R. Akhmetvaleev and L. M. Khalilov, *J. Org. Chem. USSR* (*Engl. Transl.*), **1986,** *22*, 1401
3. A. J. Cocuzza and G. A. Boswell, *Tetrahedron Lett.*, **1985**, *26*, 5363-5366.
4. W. T. Brady, S. J. Norton and J. Ko, *Synthesis*, **1983**, 1002-1005.
5. E. M. Gordon, J. Pluscec and M. A. Ondetti, *Tetrahedron Lett.*, **1981**, *22*, 1871-1874.
6. R. E. Harmon, W. D. Barta, S. K. Gupta and G. Slomp, *J. Chem. Soc.* (*C*), **1971**, 3645-3650.
7. K. Imafuku and K. Arai, *Synthesis*, **1989**, 501-505.
8. (a) T. Asao, T. Machiguchi, T. Kitamura and Y. Kitahara, *J. Chem. Soc., Chem. Commun*., **1970**, 89-90; (b) R. E. Harmon, W. D. Barta, and S. K. Gupta, *J. Chem. Soc., Chem. Commun*., **1970**, 935-36.
9. *Bor*-Cherng Hong, Zhong-*Yi Chen* and E. S. Kumar, *J. Chem. Soc., Perkin Trans I,* **1999**, 1135-1137.
10. H. Stadler, M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **1984**, *67*, 1854-1858.
11. W. Friedrichsen, T. Debaerdemaeker, A. Boettcher, S. Hahnemann and R. Schmidt, *Z. Naturforsch.*, *B*: *Anorg. Chem.Org. Chem.*, **1983**, *38*, 504 -515.
12. H. Stadler, M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **1984**, *67*, 1379-1385.
13. H. Staudinger and E. Suter, *Ber. Dtsch. Chem. Ges*., **1920**, *20*, 1092-1105.
14. R. Huston, M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **1982**, *65*, 451-461.

15. G. A. Russell, K. D. Schmitt and J. Mattox, *J. Am. Chem. Soc.*, **1975**, *97*, 1882-1891.
16. (a) M. D. Gheorghiu, PACIFICHEM 2005, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 15-20, 2005, *The Centennial of Ketenes Symposium*, Abstract Orgn. 046; (b) L. Gong, M. A. McAllister and T. T. Tidwell, *J. Am. Chem. Soc*., **1991**, *113*, 6021-8
17. (a) Gaussian 03 Revison-B04; (b)NRT: E. D. Glendening and F. Weinhold, *J. Comp. Chem*., **1998**, *19*, 593-609; E. D. Glendening and F. Weinhold, *J. Comp. Chem*., **1998**, *19*, 610-624; E. D. Glendening, J. K. Badenhoop and F. Weinhold, *J. Comp. Chem*., **1998**, *19*, 628-646; (c) F. Weinhold *NBO-5.0 Manual*, University of Wisconsin, Madison, Wisconsin, 2001.
18. (a) S. V. Sereda, K. M. Turdibekov, Y. T. Struchkov, M. D. Gheorghiu, M. Mihai and L. Pârvulescu, *Struct. Chem.,***1993**, *4*, 333-337; (b) manuscript in preparation.
19. Spartan 06, Wavefunctions Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612
20. M. D. Gheorghiu, M. Mihai, L. Pârvulescu, A. Vaios and F. Niculescu, *Rev. Roum. Chim.*, **1987**, *32*, 979-984.K.
21. M. D. Gheorghiu, M. Mihai, L. Pârvulescu, A. Vaios and M. Elian, *Rev. Roum. Chim.*, **1987**, *32*, 1181-1186.
22. R. Sustmann, A. Ansmann and F. Vahrenholt, *J. Am. Chem. Soc*., **1972**, *94*, 8099-8105.
23. N. Houk, J. K. George and R. E. Duke Jr., *Tetrahedron,* **1974**, *30*, 523-533.
24. A. Marton, L. Parvulescu, C. Draghici, R. A. Varga and M. D. Gheorghiu, *Tetrahedron,* **2009**, in press;
25. M. D. Gheorghiu, M. Mihai and L. Pârvulescu, *Rev. Roum. Chim*., **1995**, *40*, 653-660.
26. M. D. Gheorghiu, L. Pârvulescu, C. Drăghici, M. Mihai and A. Popescu, *Rev. Roum. Chim*., **1996**, *41*, 283-289.
27. M. D. Gheorghiu, L. Pârvulescu, K. M. Turdibekov, Y. T. Struchkov, *Rev. Roum. Chim.*, **1990**, *35*, 427-435.
28. M. S. Hussain, M.-U-Haque, M. Muqtar, A. H. Al_Husaini and S. A. Ali, *J. Chem. Cryst.* **1994**, *24*, 171-174.
29. L. Parvulescu, A. Marton, C. Draghici, R. A. Varga and M. D. Gheorghiu, *Rev. Roum. Chim.*, **2006**, *51*(7-8), 615–622.
30. M. D. Gheorghiu, L. Pârvulescu, R. Ceclan, I. Manolescu, D. Constantinescu, C. Florea and M. Stănescu, *Rev. Roum. Chim*., **1988**, *33*, 83-85.
31. W. Weyler Jr., W. G. Duncan, M. B. Liewen and H. W. Moore, *Org. Synth., Coll. Vol. 6*, Wiley: New York, **1988**, 210-215.
32. J. Thiele, *Chem. Ber*, **1900**, *33*, 666.
33. G. M. Sheldrick, *Acta Cryst.,* A64, **2008**, 112-122.
34. *International Tables for Crystallography*, Vol. C., Kluwer Academic Publishers: Dordrecht, **1992**.
35. L. J. Farrugia, *J. Appl. Crystallogr*., **1997**, *30*, 565.