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Reaction of Moore's ketene (*tert*-butylcyanoketene) with 1,3-cyclopentadiene and 1,3-cyclohexadiene. Is periselectivity controlled by the dynamic of trajectories at the bifurcation point?☆

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ABSTRACT

The cycloaddition reaction of *tert*-butylcyanoketene (TBCK, Moore's ketene) with 1,3-cyclopentadiene yields the [2+2] product, namely cyclobutanone **9**. TBCK and 1,3-cyclohexadiene provide the cyclobutanone **10** and some of the ether **11**. Both reactions yielding the cyclobutanones (**9** and **10**, respectively) are reversible. Cyclobutanone **10** is converted thermally and irreversibly into the bicyclic ether **11** via a [3,3] sigmatropic rearrangement (oxo-Cope). The X-ray single crystal data for the ether **11** confirms that the CN and the ether oxygen are in a *trans* configuration. Data provided by density functional calculations at B3LYP/6-311++G(d,p) level mirror the X-ray data.
Furthermore, the relative thermodynamic stabilities (ΔG calculated at 273 °C, 1 atm) of the most relevant isomers of **10** at mPWB1K/6-31+G(d,p) level of theory is provided. Details of the transition states that: (i) leads to cyclobutanone **10** from TBCK and 1,3-cyclohexadiene, and (ii) the oxo-Cope rearrangement of cyclobutanone **10** to produce ether **11** are provided.

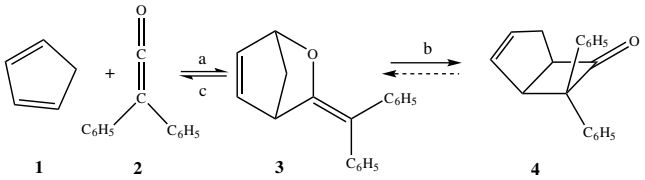
1. Introduction

The ketene cycloadditions of 1,3-cyclopentadiene (**1,3-C5**) known since 1907,[1,2] and 1,3-cyclohexadiene (**1,3-C6**), since 1937,[3] provide useful precursors allowing us to understand the mechanism of thermal [2+2] cycloaddition reactions. Cyclobutanones resulting from the cycloaddition of ketenes to **1,3-C5** have been used to access colchicine,[4] squalane synthase inhibitors,[5] a steroid,[6] and prostaglandins in an economical and stereoselective route.[7] These compounds are analogs of cytotoxic α-methylene-γ-lactones[8] that possess insecticidal, fungicidal, and nematodicidal activity.[9] **1,3-C6** as a ketenophile provides cyclobutanone precursors for the synthesis of (±)-sirenin.[10] Recently, starting from ketene adducts with cyclopentadiene, Fairlamb designed interesting ligands and catalysts.[11–13]

Since the pioneering work of Staudinger[1,2] the formation of cyclobutanones (the [2+2] reaction product) has been considered the general outcome for **1,3-C5** and **1,3-C6**. More than 65 ketenes (for **1,3-C5**) and 25 ketenes (for **1,3-C6**) are documented to afford cyclobutanones.

Recently, Machiguchi et al.,[14–16] Singleton et al.,[17] and Roberts et al.[18] have shown that cyclobutanone is not the only product of these reactions. The careful study of diphenylketene cycloaddition to **1,3-C5** conducted at low temperature revealed the formation of a cyclic ether as the primary reaction product (the [4+2] cycloaddition product), while the cyclobutanone results mostly (perhaps, not exclusively[17]) from rearrangement of the [4+2] reaction product.

It is known[15,17] that at low temperature (−20 °C) cyclopentadiene (**1**) and diphenylketene (**2**) afford a mixture containing the [4+2] cycloaddition product **3** (ca. 43% in the crude; stable at −80 °C for at least half year!) and the [2+2] cyclobutanone **4** (ca. 11% in the crude). Ether **3** is subsequently converted into the [2+2] cyclobutanone when temperature is raised to 0 °C or above.



1 2 3 4

(a) CH_2Cl_2, -20 °C; 4 h
(b) $CHCl_3$, 0 °C; 5 h, 98% or $CHCl_3$, -10 °C; 12 h, 96%; solid state 0 °C; 2.5 days, 100%
(c) CD_2Cl_2 -10 °C; 4 h: **1**(8%) + **2**(8%) + **3**(14%) + **4** (53%)

☆ Crystallographic information: CCDC 690039.

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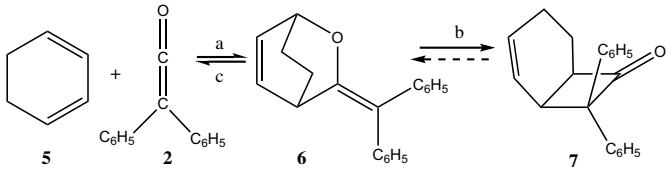
As Machiguchi et al. noticed in 1999,[15] diphenylketene reaction with **1,3-C6** yields ether **6** as the primary product, which is subsequently converted thermally into the cyclobutanone **7**. Roberts et al. were the first to document in the early 90s that 1,3-cyclohexadiene derivatives and diphenylketene give a mixture of [2+2] and [4+2] cycloadducts.[18–21]



(a) $CHCl_3$, 25 °C; 8 days
(b) benzene, 80 °C; 2 days, 98%
(c) benzene-d_6, 80 °C; 10 h: **2**(2%) + **5**(2%) + **7**(78%) + **6** (18%)

We disclose here a new situation concerning *tert*-butylcyanoketene (**TBCK**) cycloaddition to **1,3-C6**. In the case of TBCK the cyclobutanone is the primary product, which is contaminated with the isomeric ether. However, the ether becomes the major product when the cycloaddition is run in benzene at reflux, or if the cyclobutanone is heated.

Singleton et al.[17] consider that the computation of dynamic trajectories could shed light on the complex picture of the **1,3-C5** and diphenylketene cycloaddition process. The dynamic trajectories, as an alternative theoretical concept to the classical transition state, rationalize the cycloaddition reaction mechanism. The classical transition state based on statistical theory (all vibrational modes are equilibrated, e.g., intermolecular vibrational energy is redistributed fast on the time scale of the reaction coordinate path) is no longer valid. To understand the products formed, the periselectivity, and the mechanism, requires consideration of dynamic trajectories. This has been shown for the cycloadditions of **1,3-C5** with both dichloroketene and diphenylketene. The Singleton mechanism for the cycloaddition of ketenes needed to be further tested in order to understand its virtues and limitations.

We have to accept that currently there is no portable model for the cycloaddition of ketenes to 1,3-dienes or to any other ketenophile. By examining the known patterns of ketene cycloaddition to **1,3-C5** and **1,3-C6**, it appears that the electronic and steric characteristics of the substituents on the ketenes and on 1,3-diene could lead to dramatic change in the reaction pathway.

2. Results and discussion

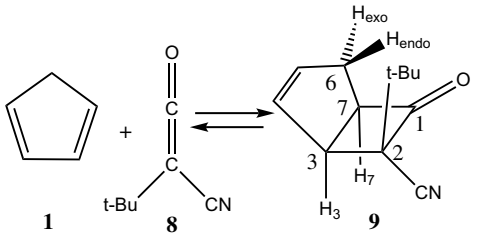
2.1. Cycloaddition of TBCK to 1,3-C5

In the reaction of the Moore's ketene (TBCK) with **1,3-C5** at 0 °C (20 h) or at reflux in benzene (4 h), the sole product is the cyclobutanone **9**. Interestingly, at room temperature cyclobutanone **9** undergoes cycloreversion: TBCK was trapped with methanol, as 2-cyano-3,3-dimethylpropionic methyl ester in addition to the cyclopentadiene dimer as evidenced by ^{1}H NMR spectroscopy.

We have designed a simple, but reliable method to predict the stereochemistry of the resulting *tert*-butylcyano substituted cyclobutanones. This method is based on the relative ^{1}H and ^{13}C chemical shifts[22–28] of some appropriate signals, which is supported by our X-ray results.[29]

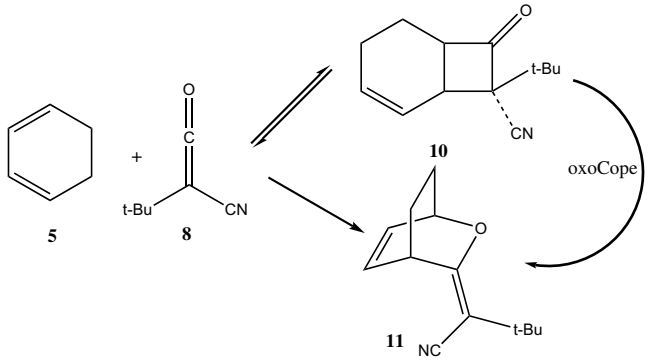
The primary NMR signatures for the *cis* configuration of the *t*-Bu group to the five-membered skeleton of cyclobutanone **9** are:

(a) The chemical shift value of the *t*-Bu protons $\delta \leq 1.1$ ppm. In cyclobutanones in which the *t*-Bu group is *trans* with respect to the larger substituent of the ketenophile, the chemical shift values of the *t*-Bu protons are $\delta \geq 1.2$ ppm.
(b) The ^{13}C chemical shift of the carbon atom from the CN group is δ=119 ppm, which is representative for a CN group facing a hydrogen atom. In cyclobutanones in which the CN group is *cis* orientated related to the bulky substituent of the ketenophile, the chemical shift of ^{13}C (CN) is approximately 114 ppm.[26,30]
(c) The bridgehead proton H_3 is more shielded (δ=3.88 ppm) than the vicinal H_7 (δ=4.23 ppm), for the reason that is orientated *cis* to the CN group. GIAO (B3LYP/6-31+G(d,p)) modelling of the chemical shifts has confirmed that H_3 is relatively shielded (4.00 ppm) with respect to H_7 (4.16 ppm).



2.2. Cycloaddition of TBCK to 1,3-C6

TBCK adds to **1,3-C6** to yield two products. At −20 °C by ^{1}H NMR spectroscopy (in toluene-d_8), the cyclobutanone **10** (by monitoring the signal at δ=3.47 ppm) is formed rapidly, while ether **11** (by monitoring the signal at δ=5.16 ppm) is present in less than 25% and stays constant for about 6 h. On warming the sample to 20 °C, the signals of cyclobutanone **10** decrease while the ^{1}H NMR signals of the ether **11** predominate in the reaction mixture. This fact suggests that both compounds are formed directly from TBCK and **1,3-C6**. However, ether **11** also results from the oxo-Cope rearrangement of cyclobutanone **10** at higher temperature. For example, in refluxing benzene for 4 h or by heating during the vacuum distillation of the cyclobutanone **10**. In order to rationalize the periselectivity, perhaps the best scenario for the cycloaddition of TBCK to **1,3-C6** is the one devised by Singleton et al.[17] for the case of diphenylketene cycloaddition to **1,3-C5**. After TBCK and **1,3-C6** reach the transition state structure, the trajectories, which evolve downhill are branched at the bifurcation point. Most trajectories end in the formation of cyclobutanone **10**, however, a few afford ether **11**. Additionally, one would expect a large number of trajectories on the cyclobutanone path that recross the transition state. Some more details concerning the potential energy surface will be commented in Section 2.2.4.



The *t*-Bu group from the cyclobutanone **10** is *cis* to the cyclohexene skeleton (inferred from the NMR spectroscopic data). The oxygen from the ether **11** is *trans* to the CN group (based on X-ray

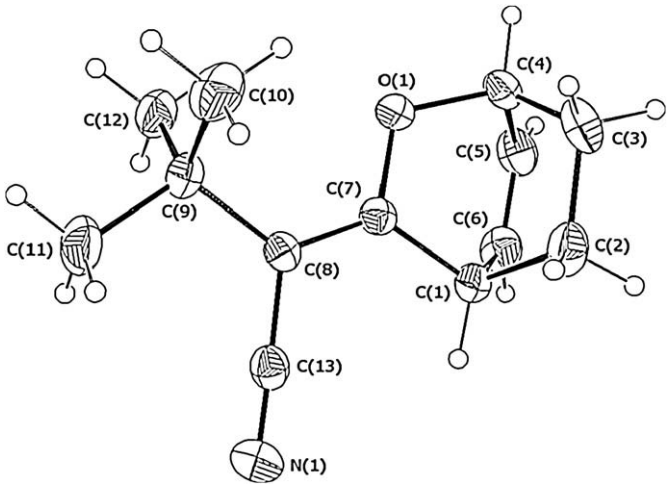


Figure 1. General view (ORTEP) of the molecular structure showing 30% probability displacement ellipsoids and the atom numbering scheme.

data, see Fig. 1). Also, it was noticed that the cyclobutanone **10**, even at room temperature, cycloreverts to TBCK and **1,3-C6**.

The oxo-Cope rearrangement is irreversible; ether **11** cannot thermally be converted to cyclobutanone **10**. *This fact is opposite to what was noticed in the diphenylketene cycloaddition to 1,3-cyclohexadiene, when (1) the ether **6** is a primary product and (2) the ether **6** rearranges thermally into cyclobutanone **7**.*[15]

The stereochemistry of the cyclobutanone **10** was assigned based on the same arguments as those taken into account in the case of the similar reaction performed with **1,3-C5** (relative chemical shifts being supported by GIAO calculations).

2.2.1. *X-ray structure of ether **11***

A single crystal of ether **11** has been subjected to X-ray measurements, confirming the structural connectivity of a 2-oxabicyclo[2.2.2]oct-5-ene skeleton. A related structure[31] has been subjected to X-ray analysis, but no details were revealed.

The most valuable information obtained from the X-ray pattern is the configuration of the double bond. The configuration of the cyano group and the vicinal oxygen atom is *trans*. This stereochemical preference is rationalized below (see 2.2.3). It is worth noting that a similar configuration provides additional stability to ether **12** versus the isomer **13**. Moreover, as it will be presented below, transition states involving TBCK display a preference for a *trans* configuration of the CN group and the oxygen atom. The calculated geometry at the B3LYP/6-311++G(d,p) level of theory acceptably agrees with the X-ray results (see Table 1).

Table 1
Significant bond distances, bond angles, and dihedral angles for ether **11**

	X-ray	B3LYP/6-311++G(d,p)
Bond distances		
O1–C7	1.342(4)	1.354
O1–C4	1.478(4)	1.473
C7–C8	1.348(4)	1.359
C7–C1	1.501(5)	1.516
C1–C2	1.544(6)	1.565
C2–C3	1.520(7)	1.550
C3–C4	1.523(6)	1.542
C4–C5	1.477(6)	1.504
C5–C6	1.320(6)	1.336
C1–C6	1.506(5)	1.516
C8–C9	1.530(5)	1.548
C8–C13	1.422(5)	1.424
C13–N1	1.141(5)	1.160
Bond angles		
O1C7C8	120.1(3)	121.0
C7C8C9	124.4(3)	125.1
C7O1C4	113.1(3)	113.3
Dihedral angles		
C4O1C7C1	−3.0(4)	0.9
O1C7C8C13	−179.9(3)	−179.3
O1C7C8C9	−0.6(5)	0.6

2.2.2. *Relative thermodynamic stability of some isomers to compound **10***

On the potential energy surface (see Fig. 2) of the **1,3-C6** cycloaddition to TBCK, we computed only four ketones (**10**, **15**, **16**, and **17**) and four ethers (**11**, **12**, **13**, and **14**). By taking cyclobutanone **10** as reference, the less thermodynamically stable isomer contains the frame of an oxetane embedded into the 8-methylene-7-oxa-bicyclo[4.2.0]oct-2-ene skeleton, as in **12** and **13**.

The relatively more stable isomer possesses the bicyclo[2.2.2]oct-5-en-2-one skeleton **17**. In our hands none of these products was ever observed as reaction product in the cycloaddition of a TBCK to **1,3-C6**. Of the experimentally observed reaction products, ether **11** is more stable than cyclobutanone **10**, with the predicted value of ΔG=−3.5 kcal/mol (ΔG=−6.3 kcal/mol at B3LYP/6-31+G level of theory).

2.2.3. *Why is the trans configuration of the oxygen and the CN group preferred?*

The X-ray results for ether **11** reveal a preference for a *trans* configuration of the oxygen and cyano group. Additionally,

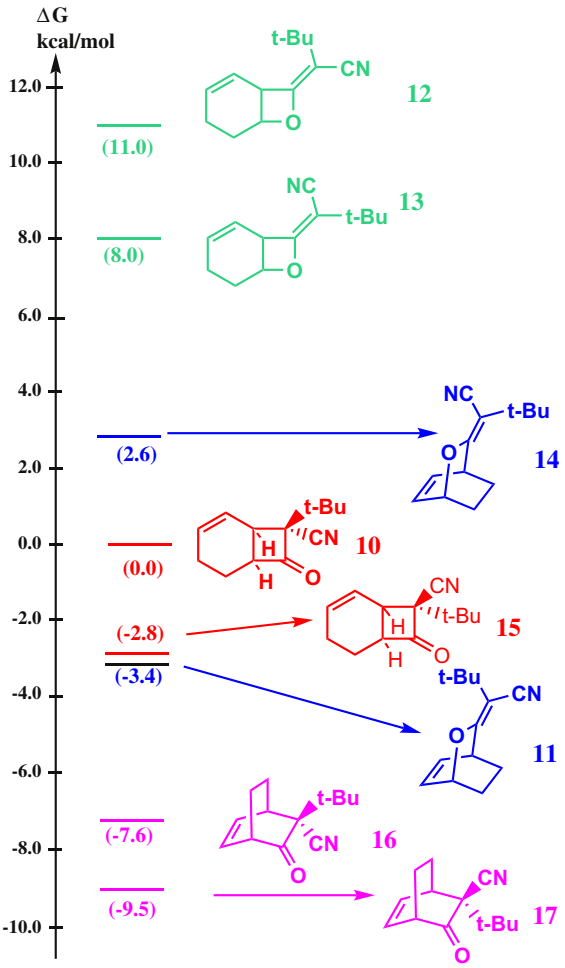
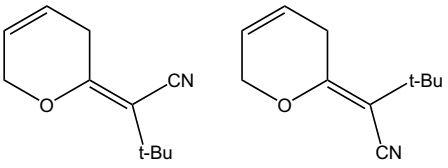


Figure 2. Calculated mPWB1K/6-31+G(d,p)[33] relative Gibbs free energies (reference cyclobutanone **10**) of ketones and ethers that are potential products of the cycloaddition of TBCK to 1,3-cyclohexadiene.

mPWB1K/6-31+G(d,p) calculations predict that the *trans* isomer is thermodynamically more stable. For example, ether **11** is more stable than the isomer **14** by ΔG=6.0 kcal/mol, while oxetane **12** is more stable than isomer **13** by ΔG=3.0 kcal/mol.

Any rationale for the *trans* configuration preference should, in part, be rooted in the extended conjugation among oxygen lone pair (LP) and the π electrons from the C=C and C≡N bonds. Natural Bond Orbital (NBO) analysis as described by Weinhold[32] is the appropriate tool to learn about the anatomy of significant electronic interactions. We have chosen as a suitable model 2-methylene-3,6-dihydro-2*H*-pyran, which is substituted on the *exo*-methylene bond with cyano and *t*-Bu groups (see Scheme 1).



Scheme 1. Computational models to understand the preference for the *trans* configuration of CN and oxygen.

Thermodynamically, the Pyran *trans* model is more stable than a Pyran *cis* configuration by ΔG=5.8 kcal/mol, which is relatively close to the difference between compound **11** (the *trans* isomer) and **14** (the *cis* isomer).

The preference for the *trans* configuration is confirmed by the computation of: (i) the second order perturbation energy, (ii) destabilization energy resulted by deleting the major interactions, and (iii) Natural Resonance Theory (NRT).

Examination of the donor/acceptor interactions (B3LYP/6-31+G, at NBO-3 level/G03W) reveals that the two most important interactions are the oxygen lone pair donation into the C=C π antibonding orbital ($LP_O/\pi^*_{C=C}$) and the C=C conjugation with the CN antibonding orbital ($\pi_{C=C}/\pi^*_{CN}$) (see Table 2).

Table 2
Second order perturbation interactions (in kcal/mol, NBO 3 calculations)

Configuration	$\pi_{C=C}/\pi^*_{CN}$ donor-acceptor	$LP_O/\pi^*_{C=C}$ donor–acceptor
Pyrane *cis*	19.7	18.8
Pyrane *trans*	22.2	24.4

The *trans* alignment of the oxygen and the cyano groups (see Table 2) provides a stronger interaction between the two donor/acceptor interactions.

The same conclusion is reached if the $\pi_{C=C}/\pi^*_{CN}$ and $LP_O/\pi^*_{C=C}$ NBO Fock matrix elements from the NBO-3 calculation at the B3LYP/6-31+G level of theory (G03W package) are deleted. The *trans* configuration is more destabilized (57.5 kcal/mol) than the *cis* configuration (50.7 kcal/mol). Therefore, within the *trans* configuration the conjugation is stronger than in *cis* configuration. The resonance weights of the resonance structures as a result of NRT analysis (NBO-5) predict also a stronger conjugation in the *trans* configuration. The NRT resonance weight of the leading resonance structure for the *trans* configuration is smaller than the NRT resonance weight of the leading structure in the *cis* configuration, meaning stronger π conjugation in the former one.

2.2.4. Transition states

An extensive search on the potential energy surface at mPWB1K/6-31+G(d,p)[33] level of theory for TBCK cycloaddition to **1,3-C6** revealed the existence of two transition states. One is the TS_1 of cyclobutanone **10** formation directly from TBCK and **1,3-C6**, and the second, TS_2, is for the ether **11** formation from the cyclobutanone **10** via an oxo-Cope reaction. We were not able to locate the TS for ether **11** formation directly from TBCK and **1,3-C6**. Therefore, it appears that cyclobutanone **10** is the primary reaction product, based on computations at the mPWB1K/6-31+G(d,p) level of theory. This is in contradiction with the experimental finding, which shows that ether **11** is also formed, however, in lesser amount (ca. 25%). To reconcile the formation of **11** directly from TBCK and **1,3-C6** would warrant a dynamic trajectories study, which is computationally extremely demanding. Unfortunately we do not have the resources for such an exercise. An interesting conclusion suggested from Figure 3 stems from the fact that the cycloreversion reaction from cyclobutanone **10** leading to TS_1 has the same $\Delta G^{\ddagger}$ (ca. 23 kcal/mol) as the height of TS_2, affording ether **11**.

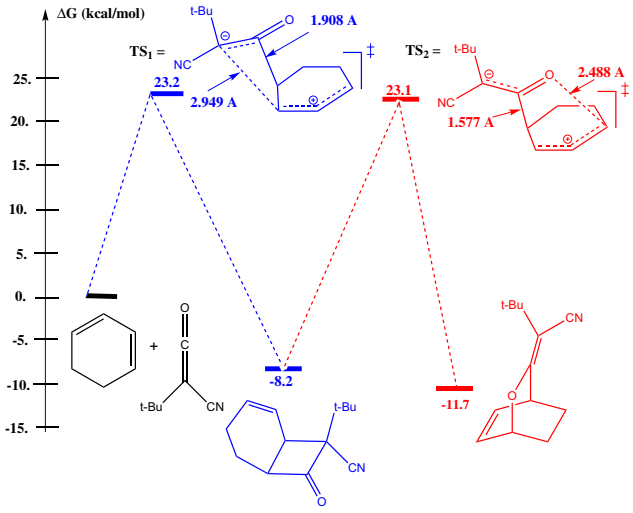
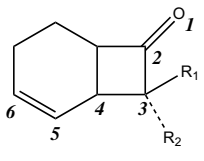


Figure 3. Predicted TS for formation of cyclobutanone **10** and the ether **11** from mPWB1K/6-31+G(d,p) computations.

The CN substituent enhances the ability of cyclobutanone **10** to undergo oxo-Cope rearrangement because of the weakening of the C_3–C_4 bond. For example, (Scheme 2), the total natural resonance theory bond order (mPWB1K/6-31+G(d,p) level and NBO-5) of the C_3–C_4 bond (cyclobutanone **10**) is 0.034 less than the same bond of cyclobutanone **10a** (R_1=R_2=H). Also, the electron density (ρ_c) at the bond critical point of C_3–C_4 bond has a lower value in cyclobutanone **10** than in cyclobutanone **10a**. The bulky *t*-Bu group of cyclobutanone **10** lengthens the C_3–C_4 bond in comparison with cyclobutanone **10b**, bringing about additional lowering of both bond order and ρ_c.



	R_1	R_2	natural bond order	ρ_c
10a	H	H	0.9844	0.2354
10b	H	CN	0.9698	0.2295
10	t-Bu	CN	0.9499	0.2210

ρ_c is the electron density at bond critical point (AIM 2000)

Scheme 2. Natural bond order and bond critical point electron density of bond C_3–C_4.

3. Conclusions

TBCK reacts with **1,3-C5** to yield only the cyclobutanone **9**, as the sole reaction product. This cycloaddition is reversible. Cyclobutanone **9** does not undergo conversion by an oxo-Cope rearrangement to an ether similar to compound **3** that would be the [4+2] cycloadduct. The outcome for cycloaddition of TBCK to **1,3-C6** is different. Cyclobutanone **10** is the major reaction product (ca.

75%) accompanied by ether **11** (ca. 25%). The ether **11** results also by a different path, namely by the oxo-Cope rearrangement, on heating the cyclobutanone **10**. The shelf life of cyclobutanone **10** is limited because it cycloreverts to TBCK and **1,3-C6**, while ether **11** is relatively robust. The structure of the ether **11** is supported by an X-ray diffraction study. Computationally (mPWB95/6-31+G(d,p)) two transition states were identified: one for the cyclobutanone **10** formation and a second for the oxo-Cope rearrangement to give ether **11**. Despite an intensive search, the transition state for the direct formation of ether **11** directly from TBCK and **1,3-C6** proved to be so far unsuccessful, standing in contrast to the result with diphenylketene cycloaddition to 1,3-cyclopentadiene.

4. Experimental section

4.1. Computational details

All computations were carried out using Gaussian 03W[34] code. Geometries of all structures were fully optimized using the hybrid meta density functional mPWB1K[33] and hybrid B3LYP[35–37] functional in conjunction with the 6-31+G, 6-31+G(d,p) or 6-311++G(d,p) basis sets. mPWB1K is proven to give good thermochemistry and thermochemical kinetics results. The keywords used to run mPWB1K with Gaussian 03W are mpwb95/basis set and IOp(3/76=0560004400). The identity of the stationary points resulted from harmonic frequency analysis as local minima (no imaginary frequency) or first-order saddle point (one imaginary frequency). The computed transition states gave only a single imaginary frequency, which when animated has the valid motion. The anatomy of donor/acceptor concerning the preference of the oxygen and cyano group to have a *trans* alignment on the *exo*-methylene double bond in ether **11** was examined using Natural Bond Orbital (computed with NBO-3[38] and NBO-5[39,40]) analysis. Natural resonance theory (NRT)[41–43] provides the weight of the contributing Lewis structure to the DFT wave function. Topological properties of the electron density were characterized using the atoms-in-molecules (AIM)[44–48] methodology. The following relevant parameters at the bond critical points (BCP, e.g., saddle point in the density between two atoms) have been examined: charge density $\rho(\boldsymbol{r}_{BCP})$, Laplacian of the charge density $\nabla^2(\boldsymbol{r}_{BCP})$ and bond ellipticity (ε_{BCP}).

4.2. Experimental

Anhydrous benzene (CHIMOPAR, S.A., Bucharest) was dried over sodium wire. NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer.

*4.2.1. 2-tert-Butyl-1-oxo-2,2a-tetrahydro-cyclobut[a]cyclopenta-2-carbonitrile (**9**)*

tert-Butylcyanoketene was generated in situ by thermolysis of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone in anhydrous benzene. 2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (1.5 g, 4.96 mmol) was decomposed in anhydrous benzene (25 mL) at reflux. A solution of cyclopentadiene (0.65 g, 9.8 mmol) in anhydrous benzene (5 mL) was added dropwise over 20 min and followed by additional reflux for 4 h. The solvent was removed and the crude reaction mixture was chromatographed on silica (150 g, Merck, Si 60) with carbon tetrachloride to elute the traces of unreacted diene. A second fraction eluted with benzene contained the cyclobutanone **9** as pale-yellow oil (1.3 g, 70%). The same product is formed after 20 h in benzene at 0 °C at the same molar ratio of the reagents. $C_{12}H_{15}ON$ (189.25): calcd C, 76.16; H, 7.99; N, 7.40. Found: C, 75.99; H, 8.05; N, 7.30%.

^{1}H NMR (300 MHz, $CDCl_3$): δ=1.05 (s, 9H, *t*-Bu), 2.43 (ddq, J=17.8, 9.6, 2.0 Hz, 1H, H_6), 2.70 (ddt, J=17.6, 5.2, 2.2 Hz, 1H, H_6), 3.88 (ddt, J=9.6, 3.3, 2.2 Hz, 1H, H_3), 4.23 (ddd, J=1.6, 8.4, 9.6 Hz, 1H, H_7), 5.81 (dq, J=5.8, 2.2 Hz, 1H, H_4), 5.87 (dq, J=5.8, 2.0 Hz, 1H, H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=200.74 (C=O), 135.59 (C_4), 127.94 (C_5), 118.93(CN), 72.45 (C_2), 60.38 (C_7), 49.38 (C_3), 35.10 (C_q-*t*-Bu), 33.39 (C_6), 26.5 (CH_3-*t*-Bu) ppm.

*4.2.2. 7-tert-Butyl-8-oxobicylo[4.2.0]oct-4-ene-7-carbonitrile (**10**) and 2-oxabicyclo[2.2.2]oct-5-en-3-ylidene-3,3-dimethylbutanenitrile (**11**)*

2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (1 g, 3.3 mmol) was decomposed in anhydrous benzene (25 mL) at reflux temperature. After cooling the mixture at 20 °C, a solution of cyclohexadiene (0.53 g, 6.62 mmol) in anhydrous benzene (10 mL) was added. It was maintained for 2 h at this temperature and for additional 60 h at 5 °C. The solvent was removed at 20 °C. The crude reaction mixture contained the cyclobutanone **10** (0.9 g) and the ether **11** (0.4 g). The pure product **10** was obtained as a second fraction by chromatography on silica (Merck, Si 60) with carbon tetrachloride. An experiment with the same molar ratio of the reagents carried out at 25 °C followed by maintaining the reaction mixture 12 h at this temperature, showed the ratio of 66% cyclobutanone **10** and 33% the ether **11**.

*4.2.2.1. Cyclobutanone **10**.* ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.18 (s, 9H, *t*-Bu), 2.02–2.15 (m, 2H, H_6), 1.50–1.65 (m, 2H, H_7), 3.47 (m, H_3), 4.08 (ddd, J=10.6, 6.3, 3.4 Hz, 1H, H_8), 6.04 (m, 2H, H_4, H_5, $J^{4,5}$=10.6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=200.04 (C_1), 132.65 (C_4), 123.92 (C_5), 120.1 (CN), 71.25 (C_2), 55.76 (C_8), 36.08 (C_3), 35.87 (C_q-*t*-Bu), 26.96 (CH_3-*t*-Bu), 21.06 (C_6), 18.40 (C_7) ppm.

If the addition of the diene was followed by additional reflux (4 h), after the solvent removal and the mixture distillation, only the ether **11** was obtained (yield 80%; mp=75 °C; bp=126 °C/4 mm). $C_{13}H_{17}ON$ (203.28): calcd C, 76.81; H, 8.43; N, 6.89. Found: C, 76.97; H, 8.61; N, 6.88%.

*4.2.2.2. Ether **11**.* ^{1}H NMR (300 MHz $CDCl_3$): δ=1.16 (s, 9H, *t*-Bu), 1.40–2.10 (m, 4H, $H_{7,8}$), 4.05 (m, J=6, 1.9, 2.8 Hz, 1H, H_4), 5.16 (m, J=4.8, 1.8, 3.8, 1.7 Hz, 1H, H_1), 6.46 (ddd, J=7.9, 4.8, 1.9 Hz, 1H, H_2), 6.50 (ddd, J=7.9, 6.0, 1.8 Hz, 1H, H_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=167.36 (C_5), 132.48 (C_3), 131.40 (C_2), 121.12 (CN), 91.02 ($C_{5'}$), 72.86 (C_1), 37.66 (C_4), 31.76 (C_q-*t*-Bu), 29.53 (CH_3-*t*-Bu), 25.64 (C_7), 20.65 (C_8) ppm.

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