Tropone Is a Mere Ketone for Cycloadditions to Ketenes

by **Junko Okamoto**[a]), **Shinichi Yamabe***[b]), **Tsutomu Minato**[c]), **Toshio Hasegawa**[a]), and **Takahisa Machiguchi***[a])

[a]) Department of Chemistry, Faculty of Science, Saitama University, Sakura-ku, Saitama 338-8570, Japan (e-mail: machiguc@chem.saitama-u.ac.jp)

[b]) Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528, Japan (e-mail: yamabes@nara-edu.ac.jp)

[c]) Institute for Natural Science, Nara University, 1500 Misasagi-cho, Nara 631-8502, Japan

Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

Tropone (**1**) reacts with ketenes **2** to yield $[8+2]$ cycloadducts, the γ-lactones **3**. The concerted $[8+2]$ cycloaddition path is formally symmetry-allowed, but we established that it is unfavorable. Careful low-temperature NMR (^{1}H, ^{13}C, and ^{19}F) spectroscopies of the reaction of diphenyl ketene (**2b**) or bis(trifluoromethyl) ketene (**2c**) with tropone (**1**) allowed the direct detection of a β-lactone intermediates **5b**,**c** and novel norcaradiene species **6b**,**c** in head-to-head configurations. The $[2+2]$ cycloadducts **5b**,**c** equilibrated with the norcaradienes **6b**,**c**. The β-lactones **5b** and **5c** were converted to the γ-lactones **3b** and **3c**, respectively, in quantitative yields. The DFT calculations showed that the concerted $[8+2]$ cycloaddition is unfavorable. The first step of the calculated reaction **1** + **2c** is a cycloaddition which leads to a dioxetane intermediate. This initial $[2+2]$ cycloadduct is isomerized to the β-lactone **5c** *via* the first zwitterionic intermediate. The β-lactone **5c** is further isomerized to the product γ-lactone **3c** *via* the second zwitterion intermediate. Thus, **3c** is not formed *via* the well-established two-step mechanism including zwitterionic intermediates but *via* a five-step mechanism composed of a $[2+2]$ cycloaddition and subsequent isomerization (*Scheme 12*).

1. Introduction. – Cycloadditions[1]) occur concertedly when the orbital overlap is in-phase, *i.e.*, is symmetry-allowed [4]. Tropone (**1**) is a trienone with 8π electrons, and the reaction between **1** and a ketene **2** [5] (for excellent reviews, see [6]) as shown in *Scheme 1* is a symmetry-allowed $[8+2]_{C=C}$ cycloaddition. The term $[8+2]_{C=C}$ denotes a head-to-head addition path where the C=C bond of **2** provides two electrons. For R = Ph, the product **3b** was identified first by *Gompper* and co-workers [7][8]. In the first work on the reaction between **1** and **2b**, structure **I** was assigned to the $[2+2]$ cycloadduct through the C(2)–C(3) bond of **1** [9]. Later, this structural assignment was corrected [7].

While the frontier-molecular-orbital (FMO) theory predicts the concerted addition path, the kinetic measurement suggested that the reaction between **1** and diphenyl ketene (**2b**) proceeds in a stepwise process including a zwitterionic intermediate **4b** (*Scheme 2*) [8]. Thus, there is a dilemma concerning the reaction mechanism: either the symmetry-allowed concerted cycloaddition (*Scheme 1*) or the stepwise path including a zwitterionic intermediate (*Scheme 2*) operates.

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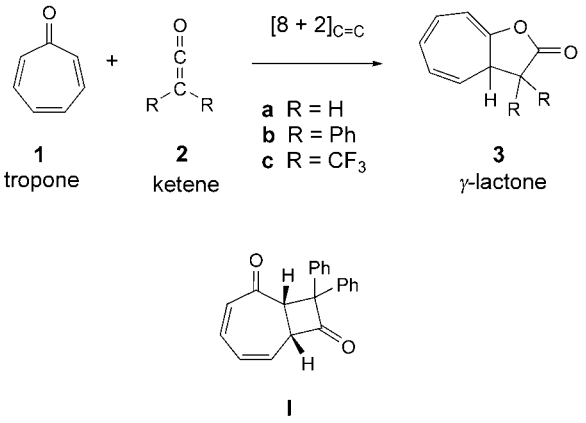
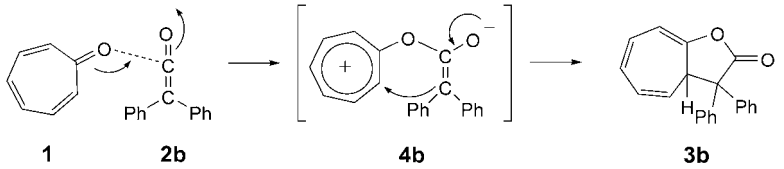
[1]) Professor *Huisgen* made an extremely brilliant achievement on cycloadditions including those of ketenes. For his autobiography, see [1]. For his representative work on ketene cycloadditions, see [2]. For reviews on cycloadditions, see, *e.g.*, [3].

Scheme 1



Scheme 2



Ketenes **2** usually react with alkenes and conjugated compounds across their C=C bonds [6][10]. A typical example is the ketene–cyclopentadiene (**A**) reaction to form a cyclobutanone **B** (*Scheme 3*, *a*[2])). We have demonstrated that the carbonyl group of the ketene adds to **A** in a *Diels–Alder* reaction and that the [4+2] cycloadduct **C** is converted to the cyclobutanone **B** in a [3,3] sigmatropic rearrangement (*Scheme 3*, *b*) [13][14].

In our recent work, the C=O group of ketene **2c** has been found to be the reaction center even for the activated alkenes **D** [15] (*Scheme 4*). A zwitterion **F** is generated not at the initial stage of the ketene–alkene reaction but by the isomerization of the $[2+2]_{C=O}$ cycloadduct, the α-methyleneoxetane **E**, to the product cyclobutanone **G**.

These findings seem to be important for us to recognize that the carbonyl groups of ketenes are not mere substituents but are reaction centers in many ketene cycloadditions. Ketenes are electrophiles, and their lowest unoccupied MOs (LUMOs), $\pi^*_{C=O}$, are FMOs. Thus, it is natural that carbonyl groups of ketenes are reaction centers toward nucleophiles. Here, the dilemma is expected to be related to the ketene C=O reaction with tropone. In other words, the tropone–ketene reaction is thought to be composed of a cycloaddition and a subsequent isomerization. What kind of cycloaddition and isomerization are involved?

To examine the reaction mechanism of *Scheme 1*, we conducted low-temperature NMR and *Fourier*-transform (FT) IR experiments. The two weight-measurable ketenes

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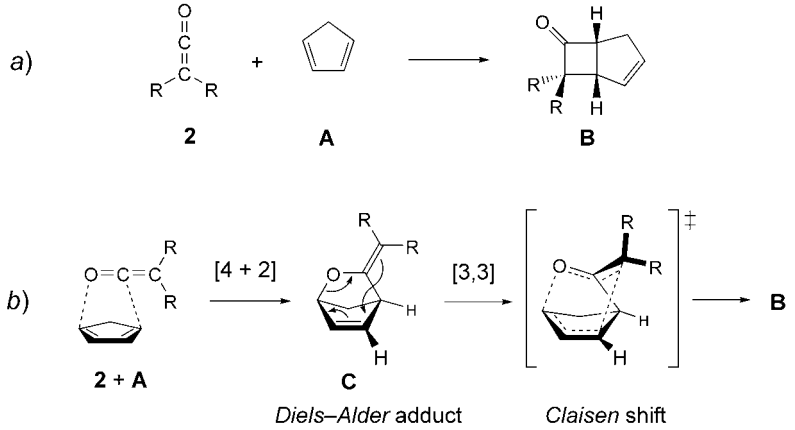
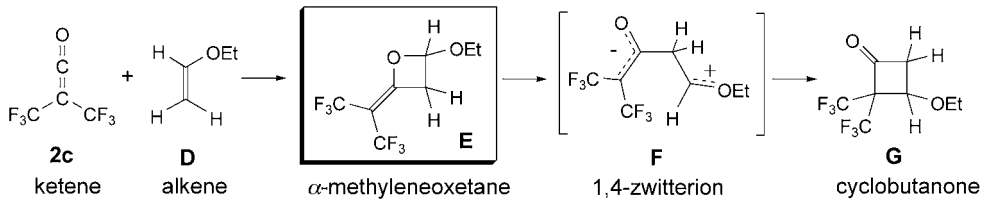
[2]) For ketene–cyclopentadiene reactions, see, *e.g.*, [11]. For ketene–open-chain-1,3-diene reactions, see, *e.g.*, [12].

Scheme 3. a) *Reaction between Ketene* **2** *and Cyclopentadiene* **A** (see [11][12]). b) *Reaction Mechanism Composed of Two Symmetry-Allowed Processes* (see [14])



Scheme 4. *Reaction between* **2c** *and an Activated Alkene, Ethyl Vinyl Ether* **D**, *Involving a Neutral Intermediate* **E** *and a Zwitterion* **F** [15]

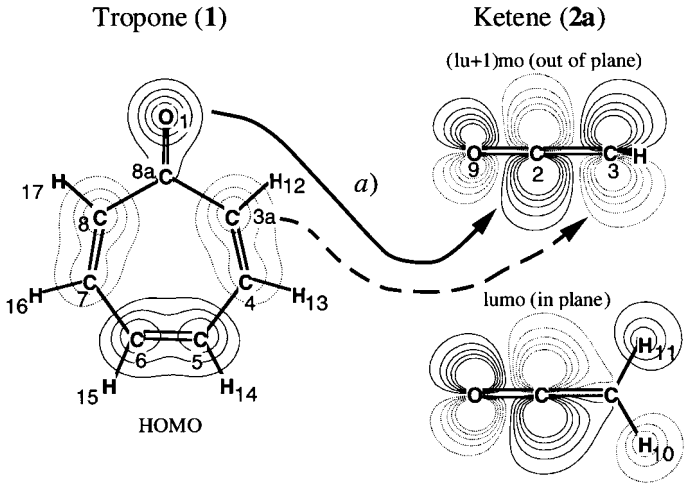


2b and **2c** were chosen for quantitative experiments. DFT Calculations were carried out to elucidate the reaction mechanism. We would like to show that the tropone – ketene reaction is essentially a ketone – ketene cycloaddition leading to novel intermediates, β-lactones with cycloheptatriene and norcaradiene structures.

2. Results of Model Calculations and the Orbital-Symmetry Rule. – The first step is to check the symmetry rule in the tropone – ketene reaction. FMO Interactions between **1** and **2a** are examined. Since the ketene is obviously an electrophile, *Scheme 5* shows its lumo and (lu + 1)mo, FMOs for a nucleophile. It is noteworthy that the (lu + 1)mo is a typical vacant orbital in cummulenes but the lumo has a shape localized at the carbonyl bond, i.e., $\pi^*_{C=O}$ in the ketene plane.

There are many orientations to make effective HOMO → lumo and HOMO → (lu + 1)mo charge transfers (CTs). Since the $[8+2]_{C=C}$ addition in *Scheme 1* appears not to take the best FMO interaction, systematic analyses of possible cycloaddition paths are required. *Scheme 6* show these models between tropone (**1**) and the parent ketene (**2a**; R = H). Nine addition paths are exhibited, the carbonyl C-atom (> C(3)=**C**(**2**)=O(9)) of **2a** is the charge-accepting center in all models. Transition state 1 obtained from **2a** (= TS1a) uses the HOMO → (lu + 1)mo CT interaction. The other eight TSs are based on the HOMO → lumo CT interaction. *Symmetry-forbidden* [2 + 2] paths, TS2a, TS3a, TS7a, and TS9a, require the homo → LUMO or homo →

Scheme 5. *Frontier-Orbital* (Charge-Transfer, CT) *Interactions for the Symmetry-Allowed* $[8+2]_{C=C}$ *Cycloaddition*

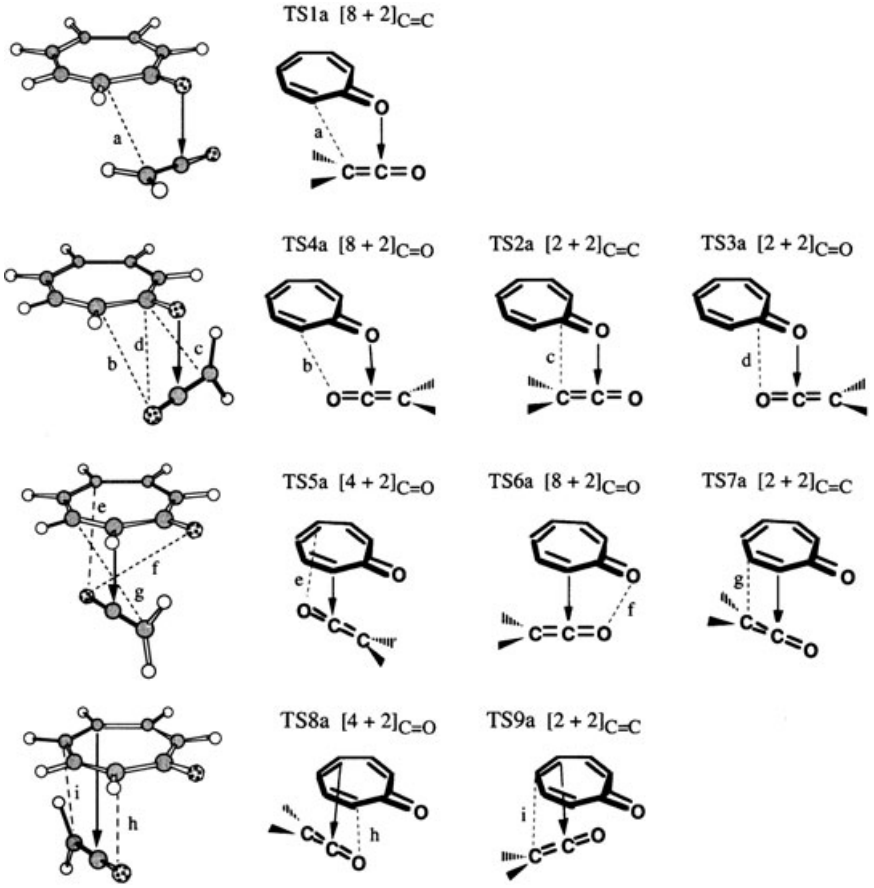


a) An arrow and a broken line indicate the interaction leading to the $[8+2]_{C=C}$ cycloaddition TS1a, in *Fig. 1*. The atom numbering follows the IUPAC nomenclature for the product **3a** (except for the H-atoms).

(LU + 1)MO back CT [16]. In view of the HOMO shape given in *Scheme 5*, the active site of tropone is the O-atom. Thus, one may predict that TS1a ($[8+2]_{C=C}$) and TS4a ($[8+2]_{C=O}$) are likely paths. If another TS has a smaller activation energy than TS1a, a subsequent isomerization will be needed to give the product **3a**. Among the nine orientations, three reaction paths are adopted since the O(1) ··· C(2) linkage is primarily formed through effective HOMO → lumo and HOMO → (lu + 1)mo CTs. *Fig. 1* shows three favorable TS geometries ($E_a < 27$ kcal/mol). Five other TSs (TS5a, TS6a, TS7a, TS8a, and TS9a) were ruled out on the basis of the activation energies (30 – 50 kcal/mol) by preliminary calculations. TS4a is of the smallest activation energy ($E_a = 17.0$ kcal/mol). However, the cycloadduct of TS4a has no reaction channel toward **3a**. TS4a is ruled out by the absence of the subsequent isomerization path.

The calculated activation energies are 26.5 kcal/mol for TS3a, 24.6 kcal/mol for TS1a, and 21.5 kcal/mol for TS2a. Noteworthy is that the 'symmetry-forbidden' $[2+2]_{C=C}$ cycloaddition is more favorable than the 'symmetry-allowed' $[8+2]_{C=C}$ one. Formally, the γ-lactone **3a** is obtained by the concerted $[8+2]_{C=C}$ addition *via* TS1a. However, the calculation showed that the concerted path is unfavorable and a stepwise path involving some other cycloadducts is predicted. Although TS2a with the smallest activation energy appears to be likely, it would suffer steric crowd in the case of the substituted ketenes **2b** (R = Ph) and **2c** ($R = CF_3$). TS3a with the largest activation energy is almost free from steric crowd. Through the model calculations (*Fig. 1*), the tropone – ketene reaction is thought to involve various steps toward the final product, the γ-lactone **3**. That is, the reaction would be different from many other tropone reactions [17]. In *Sect. 3*, the experimental search for intermediates will be described.

Scheme 6. *Nine Cycloaddition Models for Transition-State Searches*



a) Arrows show dominant CT interactions, and broken lines (a – i) indicate minor ones. TS = transition state; 'a' in TS1a – TS9a means that the parent ketene (**2a**; R = H, represented by ····· and ▬◀).

3. Experimental Examination. – We traced the reaction of tropone (**1**) with diphenyl ketene (**2b**) [18] in CH_2Cl_2 at room temperature, which gave the γ-lactone **3b** [7] (*Scheme 7*). Similarly to bis(trifluoromethyl) ketene (**2c**) [19], the same type of [8 + 2] cycloadduct, the γ-lactone, **3c** was obtained exclusively.

We attempted to detect transient reaction intermediates to clarify the reaction mechanism. Choosing experimental conditions (*Scheme 8*) precisely, we succeeded in detecting the transient intermediates **5b** and **5c** in the reactions of tropone (**1**) with ketenes **2b** and **2c**, respectively, by low-temperature NMR (^{1}H and ^{19}F) monitoring, as exemplified by *Fig. 2* for the reaction **1** + **2c** → **5c** ⇌ **6c** → **3c**. Surprisingly, the concentrations of the head-to-tail type [2 + 2]-cycloadducts, the β-lactones **5c** ⇌ **6c**, exceeded more than 80% of the total amount of the reaction mixture at a certain stage (0°, 1 h; see *Fig. 2*). The cycloheptatriene spiro β-lactones **5b** and **5c** equilibrated with their

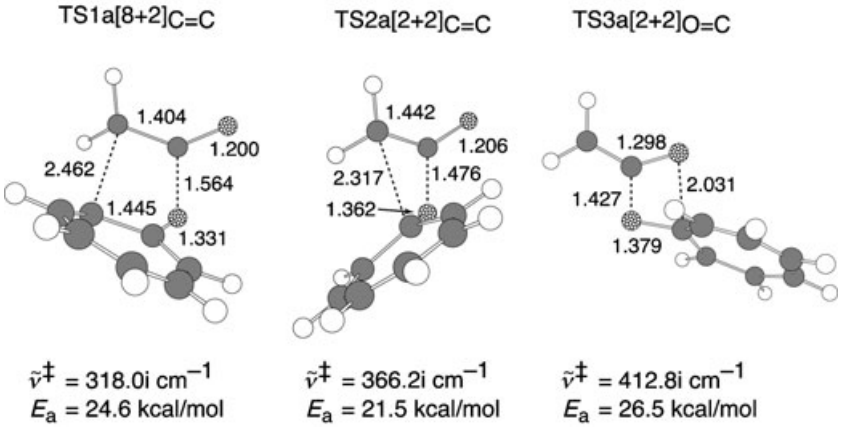
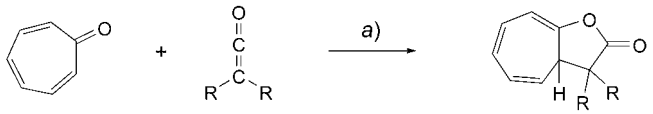


Fig. 1. *Three transition states of cycloadditions between tropone* (**1**) *and the parent ketene* (**2a**; R = H). Geometries were optimized with B3LYP/6-31G* calculations. Distances are in Å. $\tilde{\nu}^{\ddagger}$ is the sole imaginary frequency, which verifies that the obtained geometry is that of the TS.

Scheme 7. *Reactions of Tropone* (**1**) *with Diphenyl Ketene* (**2b**) *or Bis(trifluoromethyl) Ketene* (**2c**) *Giving the [8 + 2] Cycloadducts* **3b** *and* **3c**



1 **2b** R = Ph, **2c** R = CF_3 **3b** R = Ph, **3c** R = CF_3

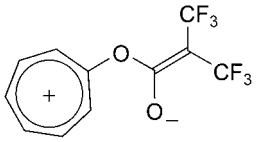
a) **1** (1 equiv.), **2** (1.1 equiv.), CH_2Cl_2, r.t., 2 h; **3b**: 96% (isolated yield); **3c**: 99% (isolated yield).

norcaradiene[3]) spiro β-lactones **6b** and **6c**, respectively (*Scheme 8*). At temperatures above $-40°$ for **5b** and 0° for **5c**, the β-lactones were converted quantitatively to the final γ-lactones **3b** and **3c**, respectively.

The detection of the initially formed intermediates **5b** and **5c** established the reaction scheme **1** + **2** → **5** → **3**. Apparently, the conventional two-step formation of the final [8 + 2] cycloadduct **3b** *via* the zwitterion **4b** in the reaction of **2b** and **1** according to *Scheme 2* does not take place; **4b** was not detected by the low-temperature NMR monitoring. On the other hand, in the reaction **1** + **2c**, a zwitterion **4c** was observed in trace amounts (see *Exper. Part*) at $-70°$; but its ^{1}H- and ^{19}F-NMR signals ($(CF_3)_2C=$, not $(CF_3)_2C<$) disappeared on warming to $-65°$; the signals due to **5c** were generated gradually. The intermediate **4c** will be discussed in *Sect. 4*.

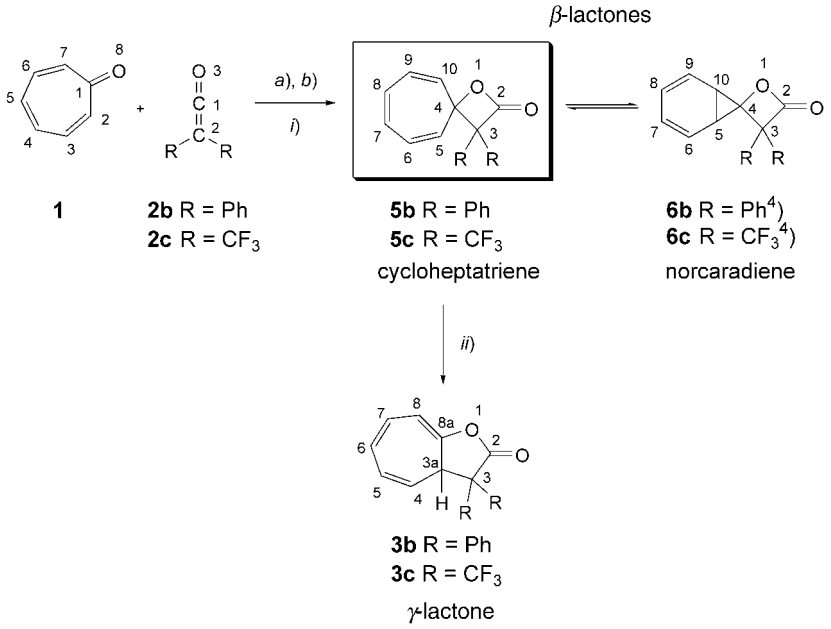
The low-temperature ^{1}H-NMR spectra of the metastable intermediate **5b** ($t_{1/2}$ ($-40°$) *ca.* 3 h) allowed us to solve the spin networks of the H-atoms of the structure. Characteristic ^{1}H-NMR patterns in the region of olefinic protons and ^{13}C-NMR signals were assigned to a cycloheptatriene moiety of **5b** and **5c**. The ^{13}C-NMR signal of the spiro atom C(4) was shifted downfield due to its direct linkage with O(1). The

[3]) For typical studies and reviews on norcaradiene, see [20].



4c

Scheme 8. *Experimental Detection of the New Intermediates* **5b**,**c** *and* **6b**,**c** *in the Reaction between Tropone* (**1**) *and Ketene* **2b** *or* **2c**



a) Equimolar amounts of **1** and **2** were mixed with CD_2Cl_2 (or (D_8)toluene) in an NMR tube. *b*) NMR detection of the transient reaction intermediates (for details, see *Exper. Part*): *i*) For **1** + **2b** → **5b**/**6b**; after 30 min at $-50°$, maximum concentration of **5b**/**6b**, 4 mol-%; for **1** + **2c** → **5c**/**6c,** after 1 h, at 0° maximum concentration of **5c**/**6c**, 83 mol-%. *ii*) For **5b** → **3b,** after 30 min at $-20°$, 100 mol-%; for **5c** → **3c**: after 2 h at 20°, 100 mol-%.

intermediates **5b** and **5c** must, therefore, be head-to-head [2 + 2] cycloadducts, *i.e.*, β-lactones which is confirmed by the spectral data. The structure of the cycloadduct **5b** was supported by comparison of its ^{1}H- and ^{19}F-NMR data with those of **5c**. The FT-IR spectra of the intermediates **5b** and **5c** showed the C=O stretching vibrations at 1832 and 1848 cm^{-1}, respectively, typical for β-lactones. In the ^{13}C-NMR spectra (100.6 MHz) of all the intermediates, the individual C-atoms were present. The ^{19}F-NMR spectra of **5c** and **3c** showed the presence of a $>C(CF_3)_2$ group (not $=C(CF_3)_2$). The detailed analysis of the NMR data was accomplished by the following techniques: resolution-enhanced ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra with *Gaussian* and sine-bell wind functions, separately [21], ^{1}H,^{1}H-COSY [22], ^{1}H,^{1}H-COLOC [23], and ^{13}C,^{1}H-COSY [24]. Thus, the presence of isomeric cycloheptatriene (**5b**-1 and **5b**-2 or **5c**-1 and **5c**-2) and norcaradiene structures (**6b**-1 or **6c**-1 and **6c**-2) was established (see *Scheme 9* and

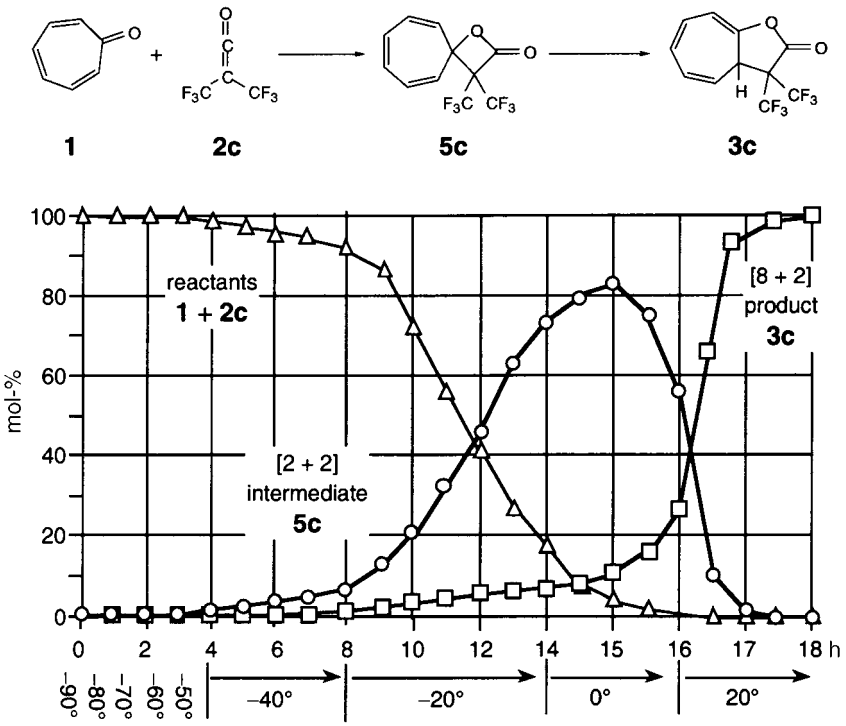
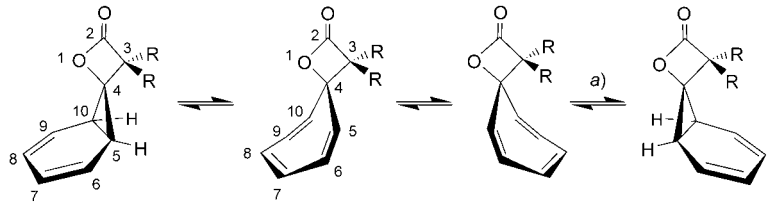


Fig. 2. *Variable-temperature ^{1}H-NMR monitoring of the reaction between tropone* (**1**) *and bis(trifluoromethyl) ketene* (**2c**) *in CD_2Cl_2*. Molar percentages for intermediate **5c** take into account the total amount of equilibrium mixture, *i.e.*, cycloheptatrienes **5c**-1 and **5c**-2 and norcaradienes **6c**-1 and **6c**-2 (see below)

Figs. 3–6); in addition to the equilibrations between the cycloheptatriene and norcaradiene structures, the conformational equilibria shown in *Scheme 9* were observed. The composite-decoupled ^{13}C-NMR spectrum of the β-lactones **5c** and **6c** at $-45°$ consisted of 28 sharp signals due to the individual seven-membered-ring C-atoms of the four isomers, which coalesced to 16 signals at higher temperature (0°) as a consequence of rapid interconversion of conformations. The ^{1}H-NMR spectra also showed similar changes. Thus, the β-lactones **5** and **6** possess a time-averaged plane of symmetry at higher temperatures, which no longer exists below $-20°$. The following ratios were determined: **5b**-1/**5b**-2/**6b**-1/**6b**-2 2.5 : 0.8 : 0.7 : 0% at $-50°$ (30 min) or **5c**-1/**5c**-2/**6c**-1/**6c**-2 45 : 24 : 11 : 3% at 0° (1 h). At elevated temperatures, the cycloheptatriene key intermediates **5b** and **5c** existed preferentially.

Asao et al. reported a trace (5%) amount of the heptafulvene by-product in the reaction between 2-methoxytropone (**1**-OMe) and **2b**, the by-product arising from decarboxylation of the β-lactone **5d** (*Scheme 10,a*) [25]. Thus, the decarboxylation from **5b** was investigated; however, even at high temperature, no CO_2 elimination was observed in the reaction of **1** with **2b** (*Scheme 10,b*). The absence of decarboxylation in the reactions **1** + **2b** and **1** + **2c** will be discussed in *Sect. 4*.

Scheme 9. *Equilibria of Isomeric Cycloheptatriene and Norcaradiene Intermediates* **5** *and* **6**, *respectively*



6b-1 R = Ph **5b**-1 R = Ph **5b**-2 R = Ph **6b**-2 R = Ph (absent)[a])
6c-1 R = CF_3 **5c**-1 R = CF_3 **5c**-2 R = CF_3 **6c**-2 R = CF_3

a) Isomer **6b**-2 is unstable owing to steric congestion between the Ph groups and the cyclohexadiene plane.

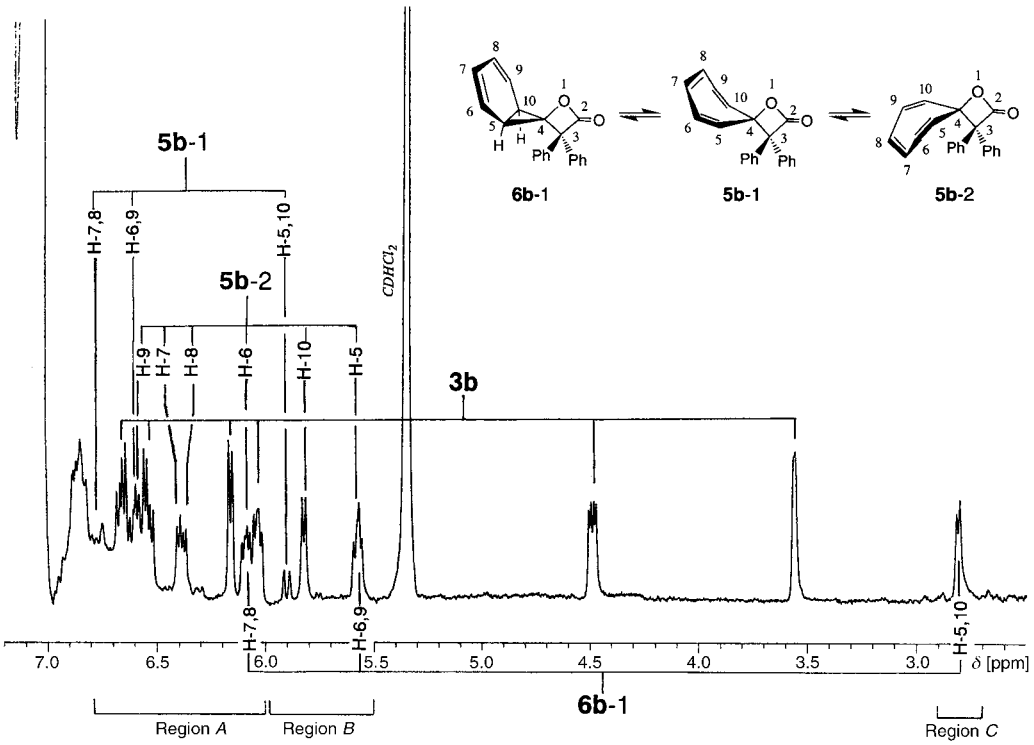


Fig. 3. *^{1}H-NMR Spectrum* (400 Mz) *of the [2 + 2]-intermediate β-lactones* (**5b**-1 ⇌ **5b**-2 ⇌ **6b**-1) *generated from the reaction between tropone* (**1**) *and diphenyl ketene* (**2b**). H-5, H-6,9, *etc.*, are short forms of H–C(5), H–C(6) and H–C(9), *etc.*[4])

4. Computational Search for Reaction Paths. – The direct formation of **5b** and **5c** *via* the $[2+2]_{C=C}$ cycloaddition (TS2) between **1** and **2b** (R = Ph) or **2c** (R = CF_3) has been predicted to be unlikely if the ketene substituents are bulky (R = Ph and CF_3). For the reaction **1** + **2c**, *Fig. 7* shows the geometries of stationary points, intermediates,

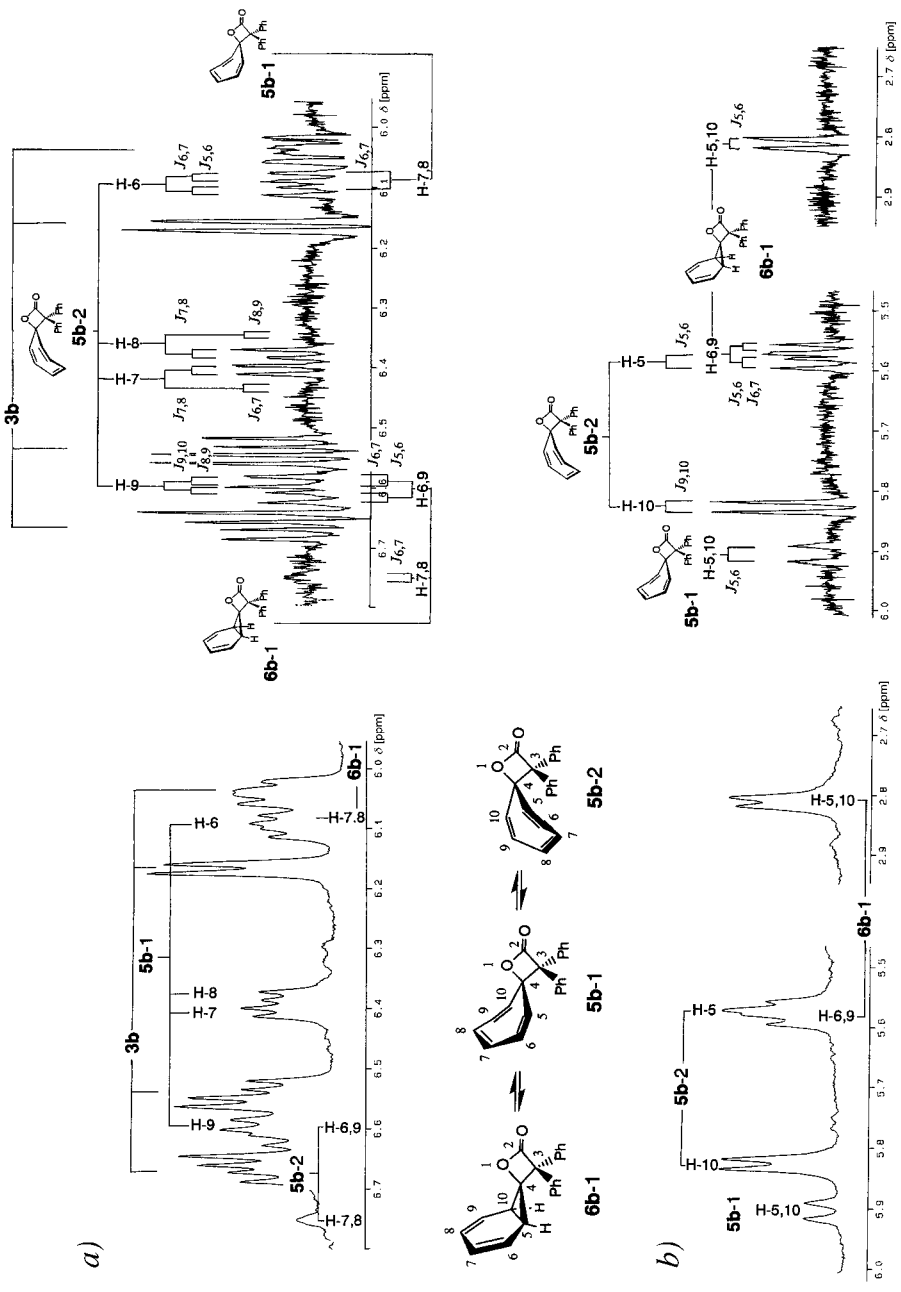


Fig. 4. a) *Expansion of* Region A (δ 6.8–6.0) *of the* ^{1}*H-NMR spectrum of* Fig. 3 (normal calibration (left) and resolution enhanced with sine-bell wind function (right)). b) *Expansion of* Region B (δ 6.0–5.5) *and* Region C (δ 2.9–2.7) *of the* ^{1}*H-NMR spectrum of* Fig. 3 (normal calibration (left) and resolution enhanced with sine-bell wind function (right)). H-6, H-7,8, *etc.*, are short forms of H–C(6), H–C(7) and H–C(8), *etc.*[4])

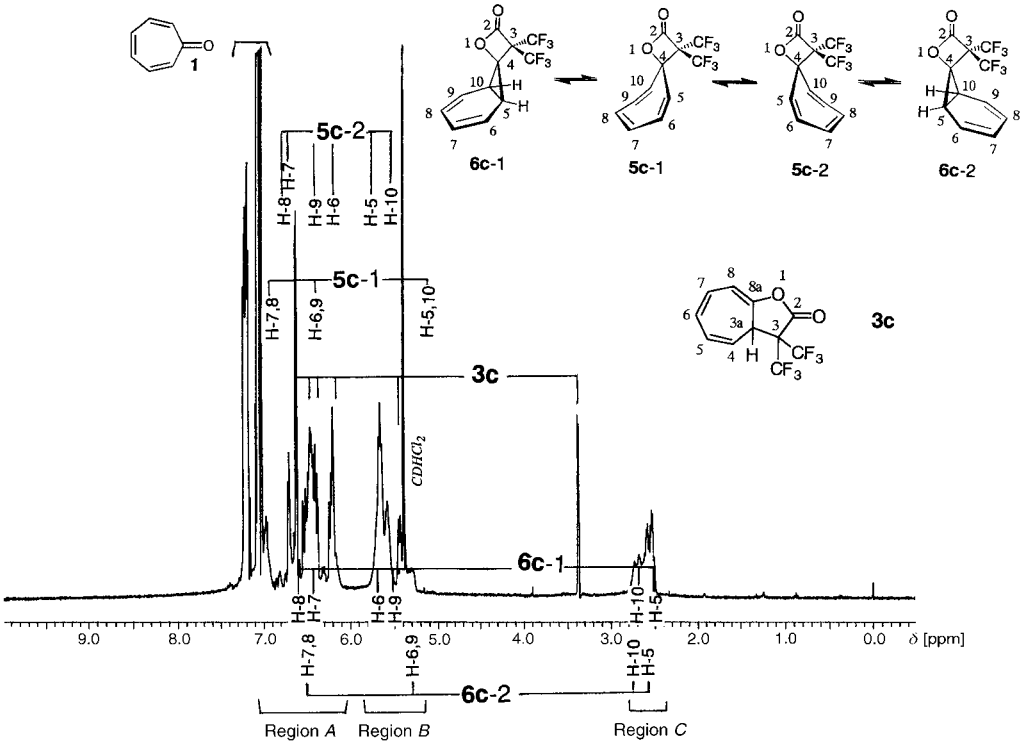


Fig. 5. *^{1}H-NMR Spectrum* (400 MHz) *of [2 + 2]-intermediate β-lactones* (**5c**-1 ⇌ **5c**-2 ⇌ **6c**-1 ⇌ **6c**-2) *generated from the reaction between tropone* (**1**) *and bis(trifluoromethyl) ketene* (**2c**). H-5, H-5,10, *etc.*, are short forms of H–C(5), H–C(5) and H–C(10), *etc.*[4])

and transition states. The first step is dioxetane formation *via* TS3c that corresponds to TS3a in *Fig. 1*. The dioxetane intermediate **7c** suffers ring strain by the exocyclic C=C bond and undergoes ring cleavage (TS10c) to give the first zwitterionic intermediate **4c**. TS10c could not be determined in the present calculations. The small geometry changes in intermediate **7c** gave intermediate **4c** since **7c** is unstable relative to the reactants (+4.9 kcal/mol) and **4c** is stable relative to them (−7.3 kcal/mol). Therefore, TS10c would be located on a very narrow region of the potential-energy surface. In **4c**, the connecting C–O bond distance is 1.526 Å. Rotation around this bond would lead to the cycloheptatriene β-lactone intermediate **5c**-2; in spite of many attempts, the ring closure TS11c could not be obtained. On ring closure, steric repulsion between a CF_3 substituent and the π-electron density of the tropone moiety must be avoided. The path would stay in an extremely limited region of the potential surface. From the β-lactone intermediate **5c**-2, the second zwitterionic intermediate **8c** is generated *via* the ring-opening TS12c. The species **8c** seems to be more stable than the first zwitterion **4c**, because the former involves an O ··· H H-bond. The zwitterion

[4]) For convenience, the β-lactones **6** are numbered similarly to the β-lactones **5**; for systematic names, see *Exper. Part.*

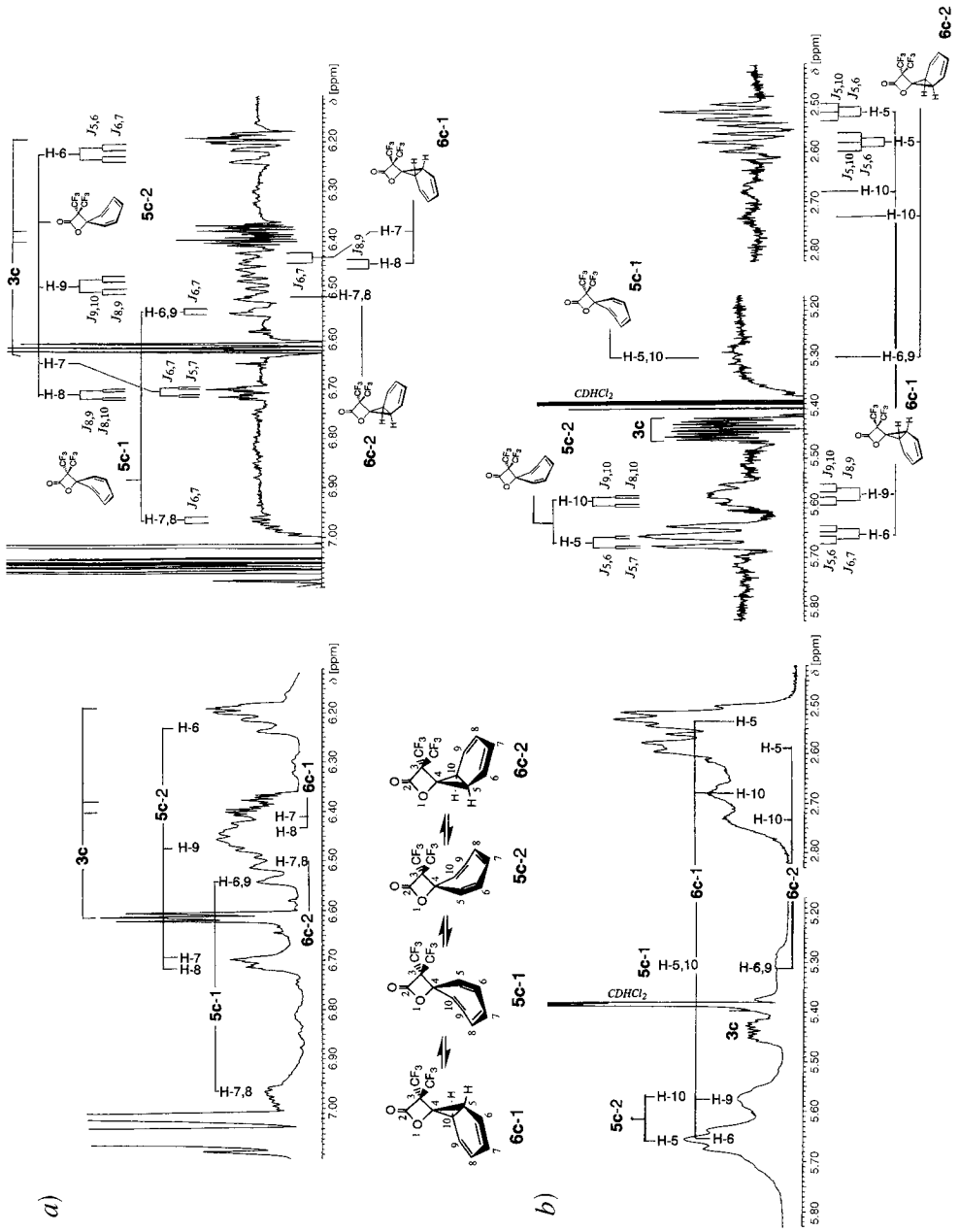
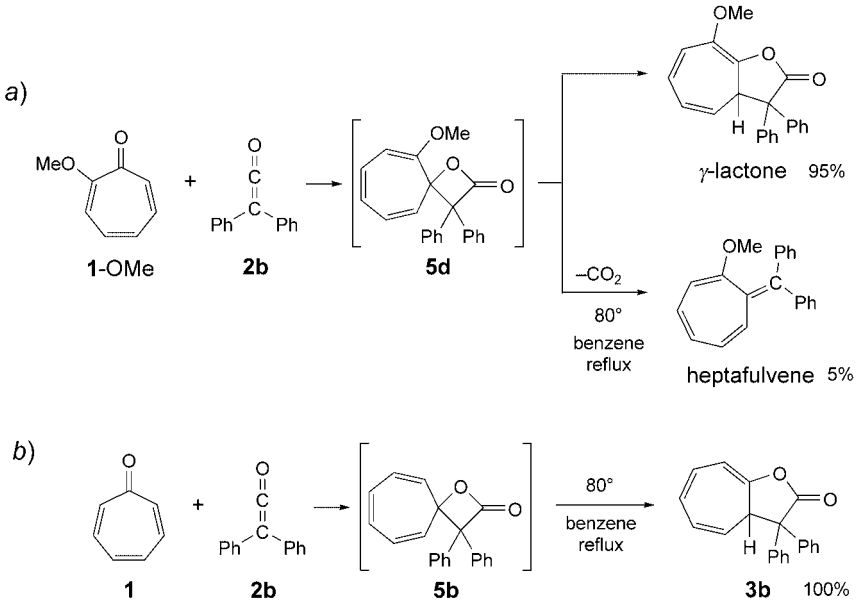


Fig. 6. a) *Expansion of* Region A (δ 7.1–6.1) *of the* ^{1}*H-NMR spectrum of* Fig. 5 (normal calibration (left) and resolution enhanced with sine-bell wind function (right)). b) *Expansion of* Region B (δ 5.8–5.2) *and* Region C (δ 2.8–2.4) *of the* ^{1}*H-NMR spectrum of* Fig. 5 (normal calibration (left) and resolution enhanced with sine-bell wind function (right)). H-6, H-6,9, *etc.*, are short forms of H–C(6), H–C(6) and H–C(9), *etc.*[4])

Scheme 10. *Examination of Decarboxylation from the β-Lactone Intermediate* (*a*) see [25]; *b*) the present work)



8c is isomerized to the final γ-lactone **3c** *via* TS13c. The intermediacy of the two zwitterions **4c** and **8c** are needed to avoid the symmetry-forbidden concerted [1,3] rearrangements **7c** → **5c**-2 and **5c**-2 → **3c**. The four-membered neutral intermediates **7c** and **5c**-2 are needed to reach the sterically congested product **3c**. In forming those neutral species, tropone (**1**) acts as if it were a simple ketone. The conjugated triene moiety in the seven-membered ring of **1** is unreactive in the initial stage, *i.e.*, in the cycloaddition.

Fig. 8 shows the energy diagram of the reaction **1** + **2c**. Although TS11c could not be obtained, it is not a rate-determining step because a C–C bond is newly formed, and no covalent bonds are cleaved. The initial cycloadduct **7c** is unstable relative to the reactants **1** + **2c**. In fact, the transient species **7c** was not detected experimentally. The stability order of the intermediates and the product is **3c** > **8c** > **5c**-2 > **4c** > **7c**. The γ-lactone **3c** is the destination as the most-stable species in the present multi-step reaction. The zwitterion **4c** was experimentally observed slightly prior to **5c**. The second zwitterion **8c** should be detected in view of its stability, but as it is in a highly excited vibrational state after TS12c, it is transformed rapidly to the product **3c** passing through the low-energy barrier of TS13c.

In *Scheme 9* (see above), the equilibria of the four isomers **5c**-1, **5c**-2, **6c**-1, and **6c**-2 are illustrated. The coexistence of **5c**-1 and **5c**-2 is due to the puckering motion of the cycloheptatriene moiety. The conformers **5c**-1 and **5c**-2 have almost the same stability; the latter is only +1.50 kcal/mol less stable than the former. However, the norcaradiene conformers **6c**-1 and **6c**-2 are +5.98 kcal/mol and +7.82 kcal/mol less stable than **5c**-1, respectively. Apparently, the equilibria in *Scheme 9* are curious in view of these energy differences. They may be explicable in terms of molecular interactions

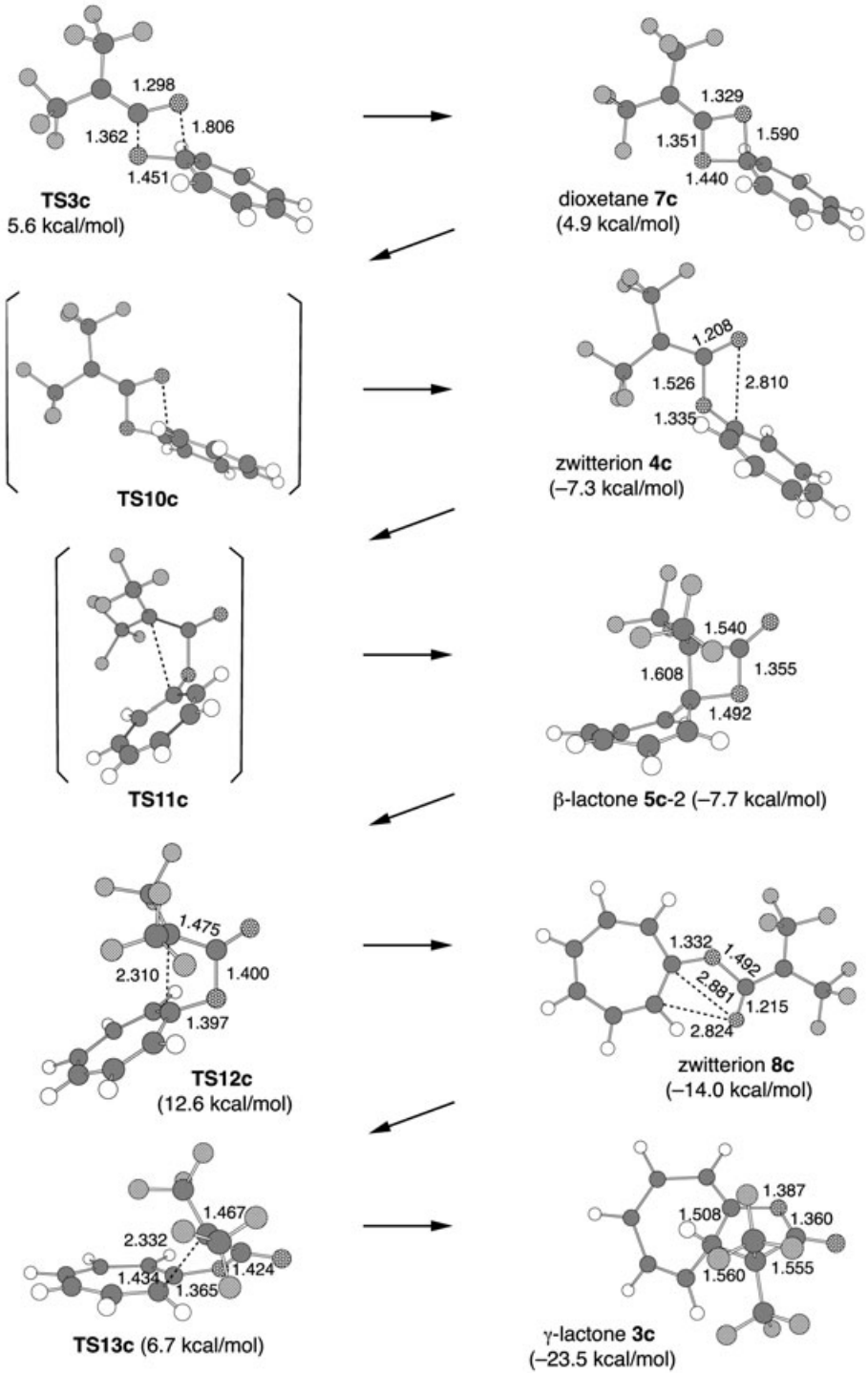


Fig. 7. *Geometries of intermediates, transition states, and the product* **3c** *of the reaction between bis(trifluoromethyl) ketene* (**2c**) *and tropone* (**1**) *optimized by RB3LYP/6-31G* SCRF = dipole.* TS = transition state; c in TS3c and TS10c – TS13c means that the ketene **2c** is used. Distances in Å.

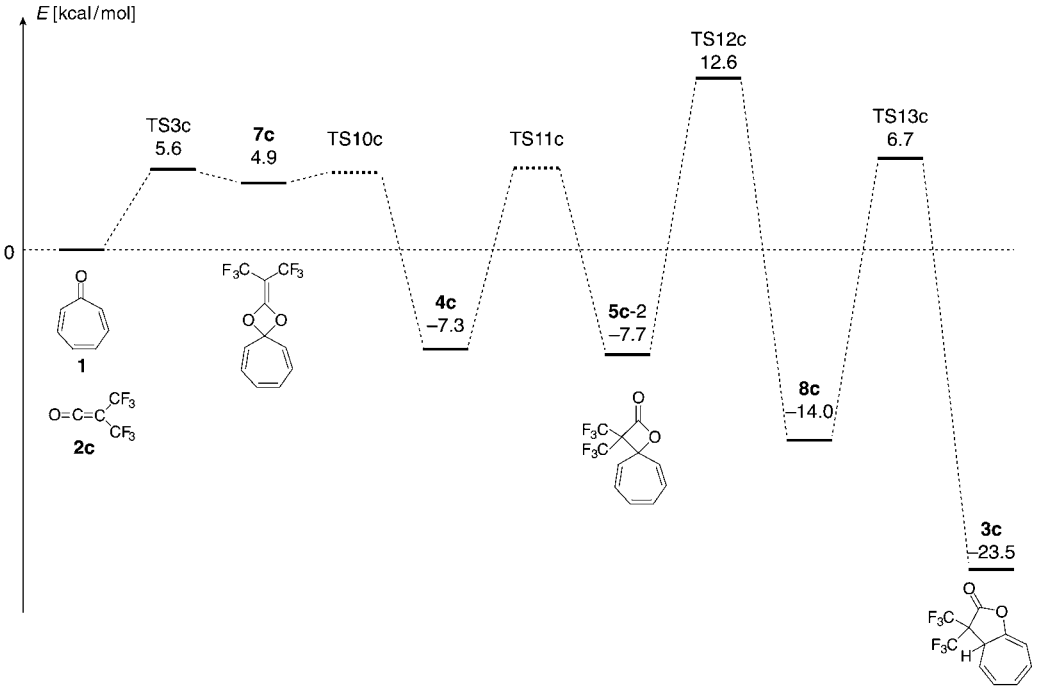


Fig. 8. *Energy changes in kcal/mol along the stepwise path corresponding to* Fig. 7 *for the reaction* **1** + **2c** → **3c**

as follows. The β-lactones **5c** and **6c** have large dipole moments (5–6 D), and their antiparallel orientation brings about a permanent dipole–dipole stabilization. At this orientation, the 4π-electron system of the norcaradiene **6c** may overlap with the 6π-electron system of the cycloheptatriene **5c** in the symmetry-allowed [6 + 4] orbital interaction (*Fig. 9*).

In *Scheme 10* (see above), the nonoccurrence of decarboxylation from β-lactones **5** (→ heptafulvene + CO_2) is illustrated. The lack of decarboxylation from **5** is also explicable in terms of this dipole–dipole interaction. The interaction fixes the cycloheptatriene ring thus blocking the geometric conversion to the heptafulvene skeleton. If the exocyclic C=C bond were formed, it would reinforce the flattening of the seven-membered ring. The formation would make the HOMO coefficient very small in the ring, and consequently the (HOMO → lumo) interaction shown in *Fig. 9* would be decreased.

In the case of the reaction of diphenyl ketene (**2b**) and tropone (**1**), presence or absence of the two zwitterions **4b** and **8b** is examined. Only the second zwitterion **8b** is obtained (see *Fig. 10*); the absence of **4b** is in accord with the experimental result. In the reaction **1** + **2b**, the β-lactone **5b** would be formed by the concerted $[2+2]_{C=C}$ cycloaddition corresponding to TS2a in *Fig. 1*. In fact, the geometry of TS2b is successfully obtained and shown in *Fig. 11*.

Through IRC calculations, TS2b is confirmed to be that of a $[2+2]_{C=C}$ cycloaddition. Indeed, the Ph group of **2b** may avoid the steric crowd flexibly (see **2b** + **D** →

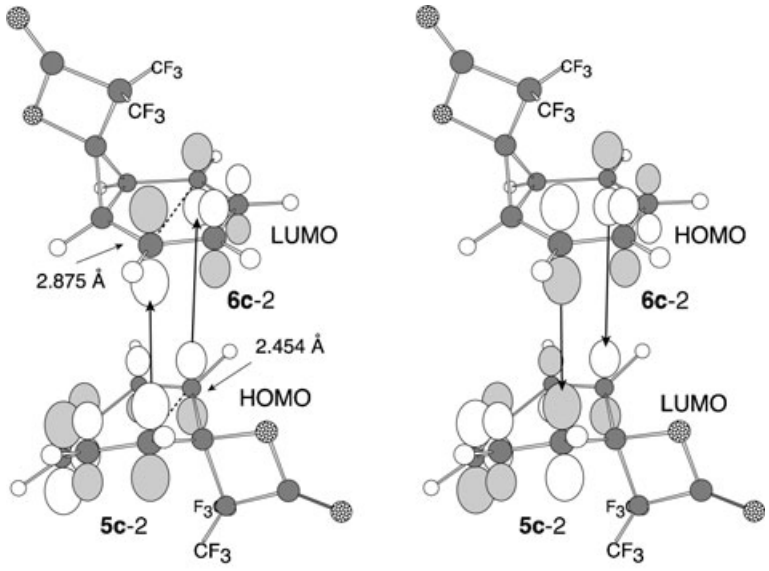


Fig. 9. *Antiparallel orientation of* **5c**-2 *and* **6c**-2 *inducing the homo* → *LUMO and HOMO* → *lumo charge-transfer interactions in the [6 + 4] symmetry-allowed orbital overlap.* Note that the terminal C ··· C distances (2.8753 and 2.4535 Å) are similar, which is suitable for the interactions

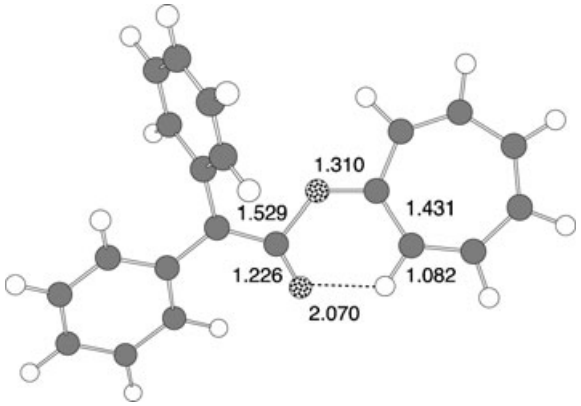


Fig. 10. *Second zwitterion intermediate* **8b** *in the reaction between tropone* (**1**) *and diphenyl ketene* (**2b**). The first zwitterion intermediate **4b** is not obtained.

H in *Scheme 11*) which is crucially different from the CF_3 group of **2c** (see **2c** + **D** → **E**); the difference has been reported in our recent work [15]. The second zwitterion **8b** needs to intervene between the β-lactone **5b** and the product γ-lactone **3b**. However, the DFT calculations demonstrate that the β-lactone **5** is the key intermediate, irrespective of the reactant ketene **2a**, **2b**, or **2c**.

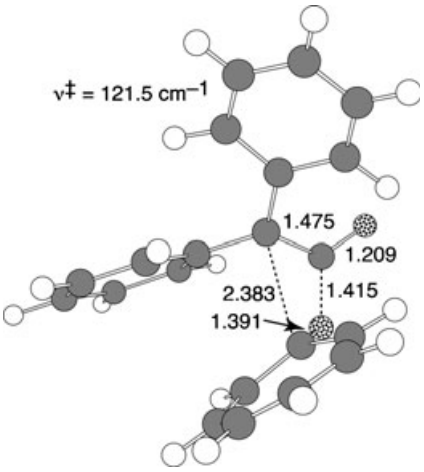
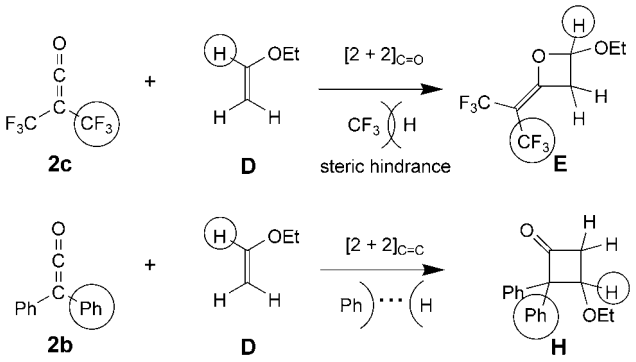


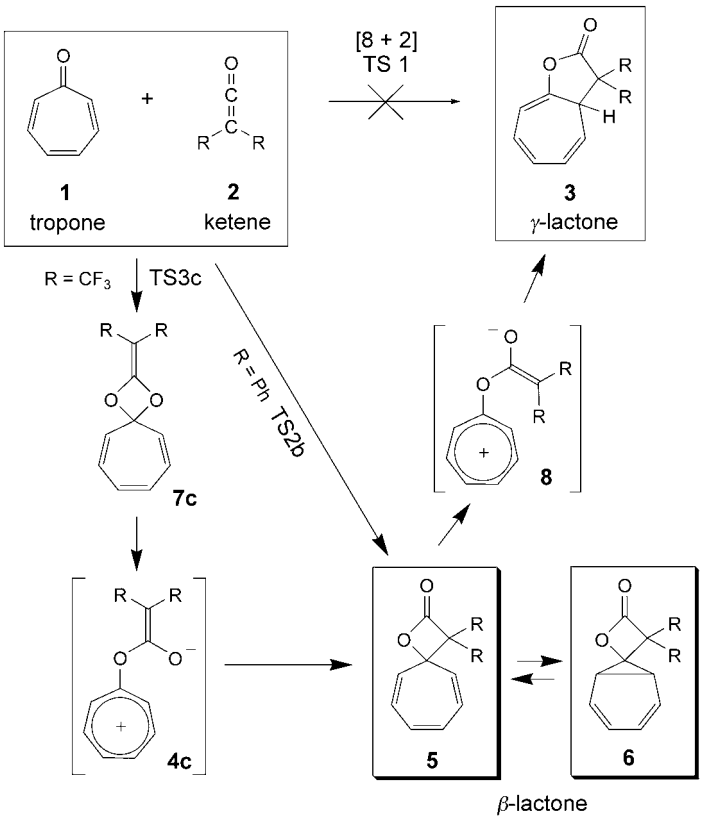
Fig. 11. *[2+2]$_{C=C}$ Cycloaddition* (TS2b) *geometry composed of tropone* (**1**) *and diphenyl ketene* (**2b**). TS2b affords the β-lactone **5b**.

Scheme 11. *Difference of Steric Crowd in the Formation of Cycloadducts from* **2b** *and* **2c**. Cyclobutanone **H** is formed from **2b** and **D**; an increase of the steric crowd in the course of the cycloaddition of **2c** and **D** leads to an α-methyleneoxetane **E**



5. Concluding Remarks. – In this work, reactions between tropone (**1**) and ketenes **2** were investigated theoretically and experimentally. Although symmetry-allowed, the concerted [8+2] cycloaddition leading directly to the γ-lactone products **3** is unfavorable. Novel [2+2] cycloadducts, the β-lactones **5** were found as key intermediates. Thus, tropone (**1**) acts as a mere ketone for ketenes, which represents an unprecedented reaction in tropone chemistry [17]. As illustrated in *Scheme 2*, the formation of a zwitterionic intermediate has been suggested by kinetics [8]. But the intermediate species is the β-lactone **5**, and the zwitterion is a transient species in the course of the isomerization **5** → **3**. Experimental low-temperature NMR analyses were consistent with the computational data. The β-lactones **5** and **6** with the isomeric cycloheptatriene and norcaradiene structures were unequivocally detected. *Scheme 12* summarizes the presented results.

Scheme 12. *New Mechanisms for the Cycloaddition between Tropone* (**1**) *and Ketenes* **2** *Established in This Work* (revision of *Schemes 1* and *2*)



Experimental Part

General. Diphenyl ketene (**2b**) [26], bis(trifluoromethyl) ketene (**2c**) [18], and tropone (**1**) [27][28] were prepared according to literature methods. Freshly distilled **2b**, **2c**, and **1** were used for the reactions. The solvents used for the reactions were freshly distilled under N_2 from appropriate drying agents, and all acids were removed carefully [29]. All reactions and their NMR monitorings were performed under either an inert atmosphere or high vacuum ($< 10^{-4}$ Torr); solns. were degassed by three successive freeze-pump-thaw cycles at 10^{-4} Torr. NMR Tubes for sealed-tube experiments were flame-dried under vacuum immediately prior to the experiments. Column chromatography (CC): *Merck* silica gel *60* (70–230 mesh); elution with CH_2Cl_2. M.p.: *Büchi 511* apparatus; uncorrected. UV/VIS Spectra (EtOH): *Hitachi U-3300* spectrometer; 1-cm quartz cell; λ_{max} in nm. IR Spectra: *Hitachi 260-50* grating spectrometer for routine spectra; *Jeol JIR-100* FT-IR instrument for FT spectra (CH_2Cl_2); $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker AM-400* (400 (^{1}H), 100.6 (^{13}C), and 376.5 MHz (^{19}F) spectrometer; CD_2Cl_2 solns., unless otherwise specified; chemical shifts δ in ppm rel. to $SiMe_4$ (=0 ppm) for ^{1}H and ^{13}C, and C_6F_6 (= – 162.9 ppm) for ^{19}F; *J* values in Hz; assignments by ^{1}H{^{1}H} homonuclear decoupling, ^{13}C{^{1}H} heteronuclear decoupling, and 2D experiments. MS: *Jeol DM-303* double focusing spectrometer; in *m*/*z* (rel. %). Elemental analyses were performed at the microanalytical laboratory, of *Daikin Industries*, Osaka, Japan.

Method of Calculation. Geometry optimizations were carried out by the DFT method. Vibrational analyses of the method were also performed to check whether the obtained geometries are at stable points or at saddle points. The DFT method was *Becke*'s three-parameter hybrid functional [30] that consists of

HF + nonlocal exchange and correlation parts (B3LYP/6-31G* SCRF = dipole). SCRF = dipole means the solvent effect of the *Onsager* reaction field model [31]. The self-consistent reaction-field method used the dielectric constant $\varepsilon = 9.08$ of the solvent CH_2Cl_2. Reaction paths were traced by the use of the IRC (intrinsic reaction coordinate) method [32]. All the calculations were carried out with GAUSSIAN 98 [33] installed at a *Compaq ES40* computer (Information Processing Center, Nara University of Education, and Computer Center of Nara University).

Reaction of Tropone (**1**) *with Diphenyl Ketene* (**2b**): *3,3a-Dihydro-3,3-diphenyl-2*H-*cyclohepta[*b*]furan-2-one* (**3b**). In a typical experiment, a soln. of **1** (1.98 g, 18.7 mmol) in CH_2Cl_2 (10 ml) was added dropwise at 0° to a soln. of **2b** (3.86 g, 19.9 mmol) in CH_2Cl_2 (30 ml). The mixture was stirred at r.t. for 2 h until the reaction was complete. Solvent removal gave a residue which was purified by a short CC followed by recrystallization from EtOH: **3b** (5.40 g, 96%) (IR and ^{1}H-NMR: identical with those of an authentic sample obtained according to [7][9] (in benzene at r.t. overnight)). Colorless prisms. M.p. and mixed m.p. 108–109° ([8]: m.p. 108–109°). UV/VIS: 280 (3.39). IR (KBr): 1800v*s*, 1640*s*, 1122v*s*, 1102v*s*, 699v*s*. ^{1}H-NMR ($CDCl_3$): 7.41–7.25 (complex *m*, 10 arom. H); 6.55 (*dd*, *J* = 11.1, 6.3, H–C(7)); 6.44 (*dd*, *J* = 11.1, 5.8, H–C(6)); 6.09 (*dd*, *J* = 6.3, 1.4, H–C(8)); 6.01 (*ddd*, *J* = 9.7, 5.8, 1.7, H–C(5)); 4.54 (*dd*, *J* = 9.7, 4.3, H–C(4)); 3.65 (*ddd*, *J* = 4.3, 1.7, 1.4, H–C(3a)). ^{13}C-NMR ($CDCl_3$): 174.95 (*s*, C(2)); 142.81 (*s*, Ph); 141.29 (*s*, Ph); 138.90 (*s*, C(8a)); 129.07 (*d*, 2 C, Ph); 128.84 (*d*, 2 C, Ph); 128.77 (*d*, 2 C, Ph); 128.19 (*d*, Ph); 127.69 (*d*, Ph); 127.61 (*d*, C(7)); 127.52 (*d*, C(6)); 127.49 (*d*, 2 C, Ph); 126.17 (*d*, C(5)); 120.09 (*d*, C(4)); 100.56 (*d*, C(8)); 59.39 (*s*, C(3)); 48.39 (*d*, C(3a)). EI-MS (70 eV): 300 (8, M^+), 194 (100, $[M - C_7H_6O]^+$), 166 (54), 165 (48), 106 (12), 78 (4), 77 (4).

Reaction of Tropone (**1**) *with Bis(trifluoromethyl) Ketene* (**2c**). *3,3a-Dihydro-3,3-bis(trifluoromethyl)-2*H-*cyclohepta[*b*]furan-2-one* (**3c**). As described above for **3b**, with **1** (2.01 g, 19.0 mmol) and **2c** (3.59 g, 20.2 mmol) in CH_2Cl_2 (40 ml) at r.t. for 2 h: **3c** (5.34 g, 99%), after distillation under vacuum (6 Torr). An anal. sample was obtained by further bulb-to-bulb distillation. Colorless oil. B.p. 58–59°/6 Torr. UV/VIS: 277 (3.55). IR (neat): 1823v*s*, 1659*s*, 1324*s*, 1289v*s*, 1262*s*, 1218v*s*, 1178*s*, 1068*s*, 999*s*, 809*s*, 696*s*. ^{1}H-NMR ($CDCl_3$): 6.55 (*ddd*, *J* = 9.6, 6.1, 2.2, H–C(7)); 6.52 (*ddd*, *J* = 9.6, 6.2, 2.2, H–C(6)); 6.33 (*ddt*, *J* = 11.8, 6.6, 1.7, H–C(5)); 6.11 (*ddt*, *J* = 6.1, 2.2, 1.7, H–C(8)); 5.43 (*ddq*, *J* = 11.8, 4.6, 2.2, H–C(4)); 3.38 (*dt*, *J* = 4.6, 1.7, H–C(3a)). ^{13}C-NMR ($CDCl_3$): 162.10 (*s* with *q* fine structure ^3J(C,F) = 1.4, C(2)=O); 139.89 (*s*, C(8a)); 128.58 (*d*, C(5)); 128.55 (*d*, C(7)); 127.69 (*d*, C(6)); 121.93 (*s* with *qq* fine structure, ^1J(C,F) = 285.1, ^3J(C,F) = 2.7, 1 CF_3); 121.43 (*s* with *qq* fine structure, ^1J(C,F) = 285.1, ^3J(C,F) = 1.7, 1 CF_3); 114.62 (*d* with *q* fine structure, ^4J(C,F) = 3.6, C(4)); 102.86 (*d*, C(8)); 60.11 (*s* with *sept.* fine structure, ^2J(C,F) = 30.7, C(3)); 41.25 (*d* with *q* fine structure, ^3J(C,F) = 2.2, C(3a)). ^{19}F-NMR ($CDCl_3$): −70.82 (*q*, ^4J(F,F) = 10.1, CF_3); −63.75 (*q*, ^4J(F,F) = 10.1, CF_3). EI-MS (70 eV): 284 (100, M^+), 283 (7), 215 (72), 106 (21), 78 (54), 77 (10). Anal. calc. for $C_{11}H_6F_6O_2$ (284.16): C 46.50, H 2.13, F 40.11; found: C 46.22, H 2.19, F 40.39.

Low-Temperature NMR Spectroscopic Monitoring of the Reaction **1** + **2**: *General Procedure*. Tropone (**1**; 0.14 mmol), ketene **2** (0.14 mmol), and CD_2Cl_2 (or (D_8)toluene; 0.40 ml) were vacuum-transferred into an NMR tube. The temp. of the mixture was regulated in an NMR probe. The monitoring of the reactions was performed periodically at various temp. between −90° and 20°. The ^{13}C-NMR measurements were performed at a probe temp. of −90° (below −90°, the reaction does not proceed).

Monitoring of the Reaction **1** + **2b**: *3,3-Diphenyl-1-oxaspiro[3.6]deca-5,7,9-trien-2-one* (**5b**)*/3′,3′-Diphenylspiro[bicyclo[4.1.0]hepta-2,4-diene-7,2′-oxetan]-4′-one* (**6b**). According to the *General Procedure*, with **1** (15 mg) and **2b** (28 mg) and ^{1}H-NMR spectroscopy. At the initial stages of the reaction at −60°, a very minor amount of **5b**/**6b** was observed. After 4 h at −55°, **5b**/**6b** (*ca.* 1 mol-% of the total amount of the mixture) was clearly detected. At −50°, mixture contained the highest concentration of **5b**/**6b** (*ca.* 4 mol-%). Disappearance of the signals due to **5b**/**6b** was observed after 30 min at −20°, while the product **3b** was clearly detected. The absence of any product other than **3b** was established by the ^{1}H-NMR at r.t.

Data of **5b**/**6b** at −50°: FT-IR: 1832v*s*. ^{1}H-NMR: **5b**-1 (2.5 mol-%): 6.58 (*dd*, *J* = 7.0, 5.2, H–C(9)); 6.42 (*dd*, *J* = 10.3, 5.6, H–C(7)); 6.38 (*dd*, *J* = 10.3, 5.2, H–C(8)); 6.10 (*dd*, *J* = 8.7, 5.6, H–C(6)); 5.81 (*d*, *J* = 7.0, H–C(10)); 5.60 (*d*, *J* = 8.7, H–C(5)); **5b**-2 (0.8 mol-%): 6.73 (*d*, *J* = 5.6, H–C(7), H–C(8)); 6.60 (*dd*, *J* = 10.4, 5.6, H–C(6), H–C(9)); 5.91 (*d*, *J* = 10.4, H–C(5), H–C(10)); **6b**-1 (0.7 mol-%): 6.09 (*d*, *J* = 8.7, H–C(7), H–C(8)); 5.57 (*dd*, *J* = 8.7, 5.8, H–C(6), H–C(9)); 2.81 (*d*, *J* = 5.8, H–C(5), H–C(10)); **6b**-2 (0 mol-%). ^{13}C-NMR: **5b**-1: 167.51 (*s*, C=O); 136.69 (*d*, C(7), C(8)); 131.93 (*d*, C(6)); 131.92 (*d*, C(9)); 127.43 (*d*, C(5)); 127.33 (*d*, C(10)); 56.83 (*s*, C(3)); 54.46 (*s*, C(4)); **5b**-2: 167.63 (*s*, C=O); 136.66 (*d*, C(7), C(8)); 132.47 (*d*, C(6), C(7)); 129.40 (*d*, C(5), C(10)); 56.54 (*s*, C(3)); 53.37 (*s*, C(4)); **6b**-1: 165.02 (*s*, C=O); 121.98 (*d*, C(7), C(8)); 121.67 (*d*, C(6), C(9)); 58.92 (*s*, C(3)); 47.23 (*s*, C(4)); 42.01 (*d*, C(5), C(10)).

Monitoring of the **1** + **2c** *Reaction: 1-{[3,3,3-Trifluoro-1-hydroxy-2-(trifluoromethyl)prop-1-enyl]oxy}cyclohepta-2,4,6-trien-1-ylium Inner Salt* (**4c**) *and 3,3-Bis(trifluoromethyl)-1-oxaspiro[3.6]deca-5,7,9-trien-2-one*

(**5c**)/*3′,3′-Bis(trifluoromethyl)spiro[bicyclo[4.1.0]hepta-2,4-diene-7,2′-oxetan]-4′-one* (**6c**). According to the *General Procedure*, with **1** (15 mg) and **2c** (25 mg) and ^{1}H- and ^{19}F-NMR spectroscopies (results in *Fig. 2*). At $-70°$, a trace amount of **4c** was detected (< 1 mol-% of the total amount of the mixture). At $-65°$, the signals of **4c** had disappeared, while the formation of **5c**/**6c** was detected. At $-40°$, the signals due of **5c**/**6c** reached 6 mol-% of the total amount of the mixture. At $-20°$ (3 h), the formation of **5c**/**6c** (32 mol-%) was clearly established. Instead of increasing the signals of **5c**/**6c** at 0°, the mixture contained the highest concentration of **5c**/**6c** (83 mol-% of the total amount of the mixture). Remarkably, increase of the signals of **3c** was detected at 20°, while complete disappearance of the signals of **5c**/**6c** was observed after 2 h at 20°. The absence of any product other than **3c** was established by the ^{1}H-NMR at r.t.

Data of **4c** *at* $-70°$ ((D_8)toluene): ^{1}H-NMR: 6.40; 6.56; 7.46. ^{13}C-NMR (at $-90°$): 179.11; 158.74; 155.37; 149.99. ^{19}F-NMR: -51.91 (br. *s*).

Data of **5c**/**6c** *at* $-20°$: FT-IR: 1848vs. ^{19}F-NMR: -63.19 (br. *s*); -63.42 (br. *s*). ^{1}H-NMR: **5c**-1 (26 mol-%): 6.71 (*dd*, *J* = 5.0, 2.0, H–C(8)); 6.70 (*dd*, *J* = 4.8, 2.0, H–C(7)); 6.48 (*dd*, *J* = 9.2, 5.0, H–C(9)); 6.22 (*dd*, *J* = 9.0, 4.8, H–C(6)); 5.66 (*dd*, *J* = 9.0, 2.0, H–C(5)); 5.58 (*dd*, *J* = 9.2, 2.0, H–C(10)). **5c**-2 (17 mol-%): 6.97 (*dd*, *J* = 6.7, 3.3, H–C(7), H–C(8)); 6.54 (br. *d*, *J* = 9.8, H–C(6), H–C(9)); 6.51 (*m*, H–C(9), H–C(6)); 5.30 (br. *m*, H–C(5), H–C(10)); **6c**-1 (11 mol-%): 6.45 (*m*, H–C(8)); 6.43 (*d*, *J* = 10.4, H–C(7)); 5.65 (*dd*, *J* = 10.4, 5.9, H–C(6)); 5.57 (*dd*, *J* = 10.1, 5.9, H–C(9)); 2.68 (br., H–C(10)); 2.53 (*t*, *J* = 5.9, H–C(5)); **6c**-2 (8 mol-%): 6.51 (*m*, H–C(7), H–C(8)); 5.30 (br., H–C(6), H–C(9)); 2.73 (br., H–C(10)); 2.58 (*t*, *J* = 6.1, H–C(5)). ^{13}C-NMR: **5c**-1: 158.23 (*s*, C=O); 124.37 (*d*, C(9)); 122.26 (*d*, C(6)); 121.73 (*d*, C(7), C(8)); 121.41 (*q*, *J*(C,F) = 286.9, CF_3); 118.99 (*d*, C(5)); 117.18 (*d*, C(10)); 60.82 (*s* with *sept.* fine structure C(3)); 52.83 (*s*, C(4)); **5c**-2: 160.24 (*s*, C=O); 134.56 (*d*, C(8)); 134.05 (*d*, C(7)); 124.68 (*d*, C(6), C(9)); 121.53 (*q*, *J*(C,F) = 288.4, CF_3); 102.53 (*d*, C(5), C(10)); 61.22 (*s* with *sept.* fine structure, C(3)); 53.11 (*s*, C(4)); **6c**-1: 154.65 (*s*, C=O); 126.85 (*d*, C(7), C(8)); 122.28 (*q*, *J*(C,F) = 289.1, CF_3); 118.51 (*d*, C(6)); 117.04 (C(9)); 62.59 (*s* with *sept.* fine structure, C(3)); 40.80 (*d*, C(10)); 40.46 (*d*, C(5)); 36.36 (*s*, C(4)); **6c**-2: 154.83 (*s*, C=O); 124.68 (*d*, C(7), C(8)); 123.37 (*q*, *J*(C,F) = 289.2, CF_3); 102.60 (*d*, C(6), C(9)); 59.38 (*s* with *sept.* fine structure, C(3)); 36.69 (*s*, C(4)); 36.62 (*d*, C(10)); 36.36 (*d*, C(5)). ^{19}F-NMR (0°): -62.84 (*s*, **6c**-2); -63.10 (*s*, **6c**-1); -63.40 (*s*, **5c**-1); -63.59 (*s*, **5c**-2).

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