

Synthesis of Carbocycles

Synthesis of 1,2,3,4,5,6,7-Heptasubstituted Cycloheptatrienes through Cycloaddition Reactions of Substituted Cyclopentadienones

Dmitry N. Platonov,^[a] Aleksandr Yu. Belyy,^[a] Ivan V. Ananyev,^[b] and Yury V. Tomilov*^[a]

Abstract: Two schemes for synthesizing heptasubstituted cycloheptatrienes with various substituents in the ring are suggested. The first method is based on cycloaddition of 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone with substituted cyclopropenes and allows cycloheptatrienes containing two or three electron-withdrawing substituents in the molecule

to be obtained. The second method employs a cascade reaction between a substituted cyclopentadienone and appropriate vinyldiazoacetates. It allows the number of electron-withdrawing substituents to be increased to five. In all cases, heptasubstituted cycloheptatrienes are formed as just one of the possible isomers.

Introduction

Previously,^[1] we used a cascade reaction between methyl diazoacetate and dimethyl bromomaleate in the presence of pyridine in a synthesis of 1,2,3,4,5,6,7-hepta(methoxycarbonyl)cycloheptatriene (HMCC). This unique molecule has three types of reaction centers, thus a series of stereo- and regioselective syntheses of fused and cage carbo- and heterocyclic compounds can be synthesized on its basis. The most interesting of them are shown in Scheme 1.^[2]

Studies on the structures of HMCC and the stable anion formed from it^[1] have shown that the reactivity of this molecule is determined, to a considerable extent, by the presence of seven electron-withdrawing groups that on the one hand, stabilize the anion, and, on the other hand, impart the usual electrophilic nature to one of the ring double bonds that is not involved in conjugation. In this case, the majority of reactions, both with electrophiles and with nucleophiles, involve the HMCC anion.^[2]

In view of the unusual type of HMCC reactivity, it seemed interesting to perform syntheses of other representatives of heptasubstituted cycloheptatrienes containing a few electron-withdrawing groups in the molecule, including groups other than CO₂Me. Unfortunately, numerous attempts to perform cascade reactions of HMCC analogues by following a similar protocol from other diazo compounds (diazoacetone, diazoacetone-trile, 2-diazo-1,1,1-trifluoroethane) and bromomaleate deriva-

tives (bromomaleonitrile, methyl 4,4,4-trifluorobut-2-ynoate) failed. Therefore, to synthesize heptasubstituted cycloheptatrienes, we tried to use an approach employed previously to synthesize heptaphenylcycloheptatriene^[3a] by cycloaddition of 1,2,3-triphenylcyclopropene to tetraphenylcyclopentadienone. In this case, we intended to use substrates already containing electron-withdrawing groups in the molecules.

To date, in addition to this method, there are two schemes of synthesis of polysubstituted cycloheptatrienes that, only with some justifications, can be called synthetic methods. The first is the cycle extension of substituted benzenes in the reactions with diazo compounds, which allows predominantly cycloheptatrienes with donor substituents in the ring to be synthesized as a mixture of isomers.^[3b] Another method is the reaction of cyclopropenes with thiophene 1,1-dioxide, which is also used mainly for the synthesis of cycloheptatrienes with donor substituents.^[3c]

Results and Discussion

Reaction of Electron-Withdrawing Cyclopentadienones with Cyclopropenes

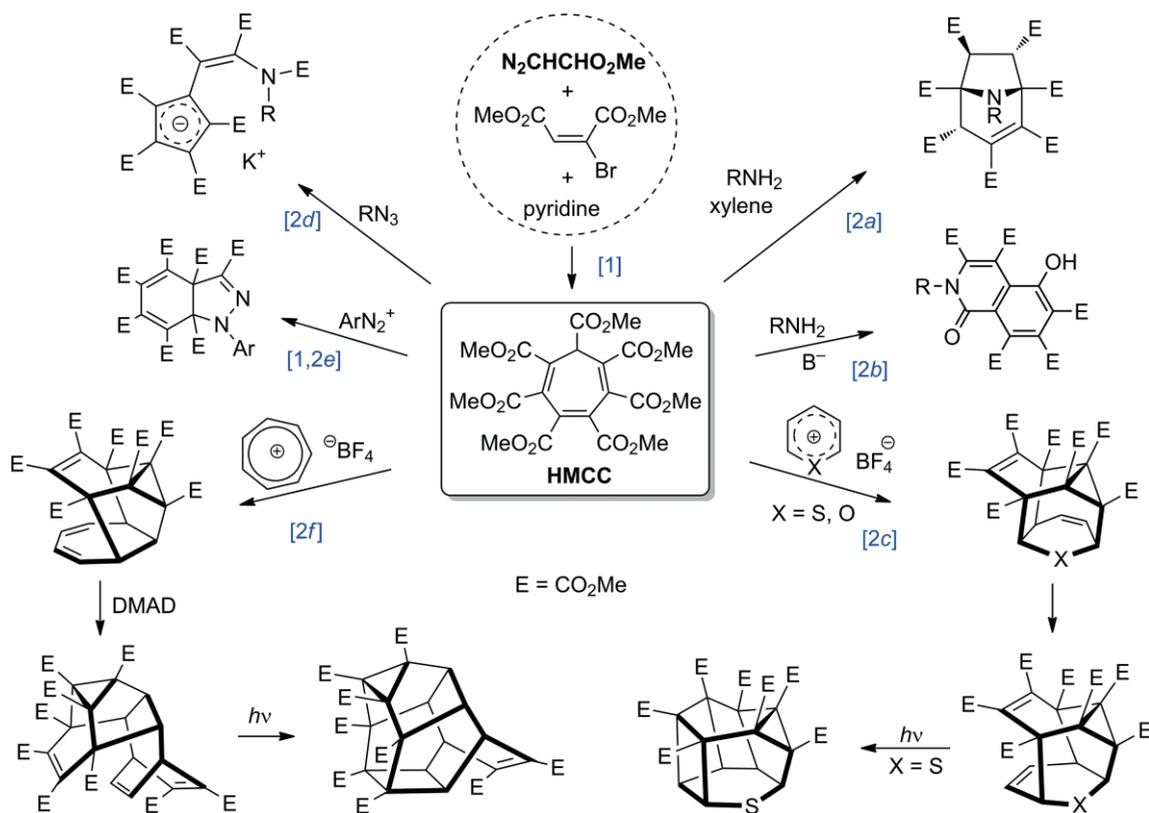
To obtain heptasubstituted cycloheptatrienes as similar as possible to HMCC, i.e., containing the maximum possible number of electron-withdrawing groups, we originally chose the clearest scheme, which included a sequence of Diels–Alder reactions between substituted cyclopentadienones and cyclopropenes followed by decarbonylation of the intermediate bicyclic adduct.

Dimethyl and diethyl 2-oxo-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylates (**1a,b**) are the most readily available stable cyclopentadienones. They can be easily obtained from the corresponding acetone-1,3-dicarboxylate and benzil.^[4] The following cyclopropenes were synthesized by using reported tech-

[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation
E-mail: tom@ioc.ac.ru
<http://zioc.ru>

[b] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 Vavilov st., 119991 Moscow, Russian Federation

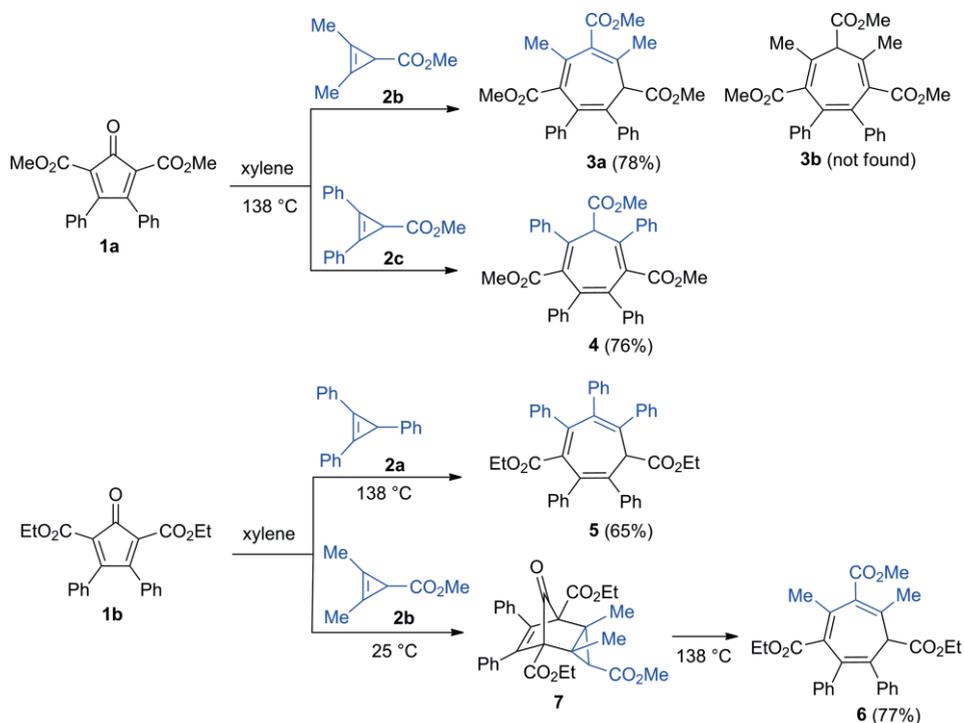
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <http://dx.doi.org/10.1002/ejoc.201600516>.



Scheme 1. Main chemical reactions based on HMCC.

niques: 1,2,3-triphenylcyclopropene (**2a**),^[5] methyl 2,3-dimethyl- (**2b**),^[6] and methyl 2,3-diphenylcycloprop-2-ene-1-carboxylates (**2c**).^[6] The reaction of dienes **1a,b** with cyclo-

propenes **2a–c** in refluxing *p*-xylene made it possible to synthesize substituted cycloheptatrienes **3–6** containing up to three ester groups in a molecule in up to 78 % yield (Scheme 2).



Scheme 2. Formation of substituted cycloheptatrienes based on cyclopentadienones **1** and cyclopropenes **2**.

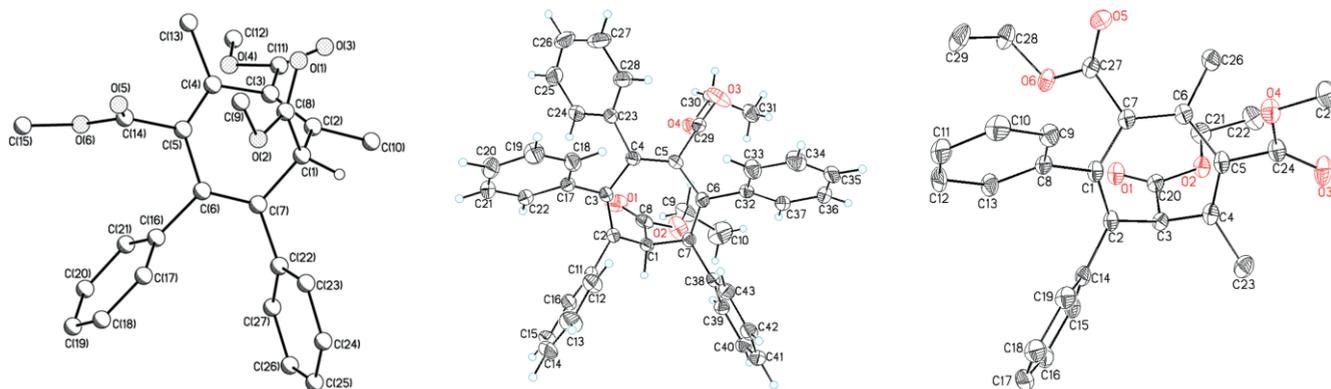


Figure 1. ORTEP-drawings for cycloheptatrienes **3a** (left), **5** (center), and **6** (right).

When we were selecting this method for the synthesis of polysubstituted cycloheptatrienes, we did not expect that if various substituents are present in the ring, the target products would be formed regioselectively as a single isomer. Nevertheless, both X-ray single-crystal analysis of compounds **3a**, **5**, and **6** (Figure 1) and ^1H and ^{13}C NMR spectra obtained for solutions of compounds **3–6** in CDCl_3 unambiguously indicated that heptasubstituted cycloheptatrienes with fixed positions of double bonds in the ring were formed. In all cases, the only ring proton was localized at the carbon atom containing an ester group. However, the fact that this proton strictly appears at a specific position in the presence of several ester groups at various positions, was unexpected.

For example, the reaction of cyclopentadienone **1a** with cyclopropene **2b** gave only cycloheptatriene **3a**, although, according to the probable scheme of the reactions, symmetric isomer **3b** would be expected to be formed. In fact, the reaction of the same cyclopentadienone **1a** with cyclopropene **2c** containing phenyl groups instead of methyl groups gave the expected symmetric cycloheptatriene **4**.

The two-stage scheme with the Diels–Alder reaction as the first stage can be confirmed by the reaction of cyclopentadienone **1b** with cyclopropene **2b** at room temperature. Based on ^1H and ^{13}C NMR spectroscopic data, formation of adduct **7** was detected. Furthermore, the latter was converted into substituted cycloheptatriene-1,3,5-tricarboxylate **6** with the same arrangement of double bonds in the ring found in the similar compound **3a** (Scheme 2). We failed to isolate pure adduct **7** because of its high lability. In this case, monitoring of the reaction mixture by NMR spectroscopy has shown that the maximum level of formation of **7** occurs in the reaction of **1b** with **2b** at $25\text{ }^\circ\text{C}$ for 30 min.

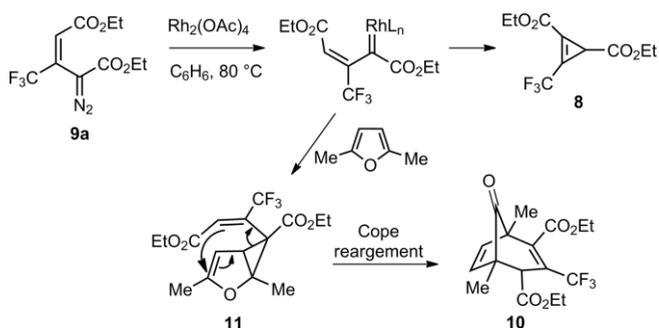
It is noted that, in almost all syntheses performed, we observed the formation of one among several possible isomers. However, according to preliminary data obtained in the study of CH-acidity of substituted cycloheptatrienes it can be assumed that not all the obtained isomers are thermodynamically favorable. The study of this problem requires more attention; in particular, the involvement of quantum-chemical calculations, which are planned to be implemented in the near future.

To increase the number of electron-withdrawing substituents in the target molecule, we performed the reaction of cyclopentadienone **1a** with the known dimethyl 2-(trifluoromethyl)cyclopropene-1,3-dicarboxylate (**8**),^[7] containing three electron-withdrawing substituents. Unfortunately, because of the electron-deficient nature of both the diene and dienophile, no reaction between them was observed. In view of this, it became necessary to search for alternative methods for synthesizing cycloheptatrienes with a large number (more than three) of electron-withdrawing substituents in the ring.

Reaction of vinyl diazoacetates with cyclopentadienones

Reaction of Vinyl diazoacetates with Cyclopentadienones

The search for new approaches to the synthesis of polysubstituted cycloheptatrienes was based on a study by Wang et al.^[7] dealing with a synthesis of 3-trifluoromethylated 8-oxabicyclo[3.2.1]octa-2,6-dienes. It has been shown that the reaction of vinyl diazoacetate **9a** with 2,5-dimethylfuran in benzene catalyzed by dirhodium tetraacetate gives, apart from cyclopropene **8**, mainly bicyclic compound **10** because of a bimolecular reaction of the rhodium intermediate (Scheme 3). The formation of vinylcyclopropane **11** is the key step in this process. It then readily undergoes a [3,3]-sigmatropic rearrangement to give 8-oxabicyclo[3.2.1]octa-2,6-diene structure **10**.

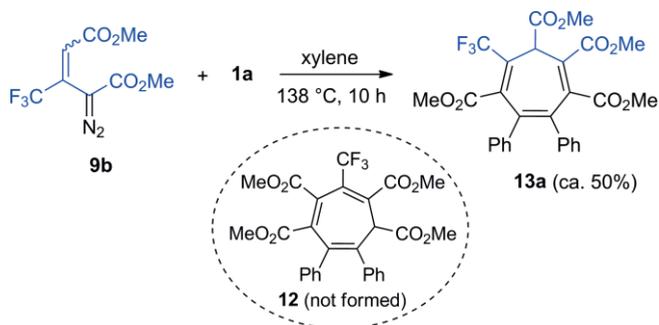


Scheme 3. Reaction of diazo compound **9a** with 2,5-dimethylfuran in the presence of $\text{Rh}_2(\text{OAc})_4$.

We assumed that if we use cyclopentadienone **1a** in this procedure instead of a furan, decarbonylation of the bicyclic ketone would give a cycloheptatriene containing five electron-withdrawing groups in the ring. Although it was hard to expect that the rhodium carbenoid would react with the electron-deficient cyclopentadienone **1**, the possibility of 1,3-dipolar cyclo-

addition of **9a** to **1** followed by dediazotization of the resulting pyrazoline to give the expected vinylcyclopropane remained. This scheme was also attractive because of the fact that reactions of 1,3-dipolar cycloaddition of diazo compounds to cyclopentadienone are known. These reactions gave pyrazolines, which actually eliminated nitrogen to give cyclopropanes on heating to reflux in benzene.^[4]

To check this hypothesis, we studied the reaction of cyclopentadienone **1a** with vinyl diazoacetate **9b** by heating the mixture to reflux in xylene. In fact, this reaction resulted in a heptasubstituted cycloheptatriene, but the positions of substituents in it were found to differ from those we expected based on the reactions of cyclopentadienone **1** with cyclopropenecarboxylates **2b,c** (Scheme 2) or by analogy with the conversion of vinylcyclopropane **11** (Scheme 3); that is, instead of the expected cycloheptatriene **12** with symmetric arrangement of substituents (neglecting the positions of double bonds in the ring), cycloheptatriene **13a** was formed (Scheme 4), as followed unambiguously from the data of X-ray single-crystal analysis (Figure 2).



Scheme 4. Reaction of diazo compound **9b** with cyclopentadienone **1a**.

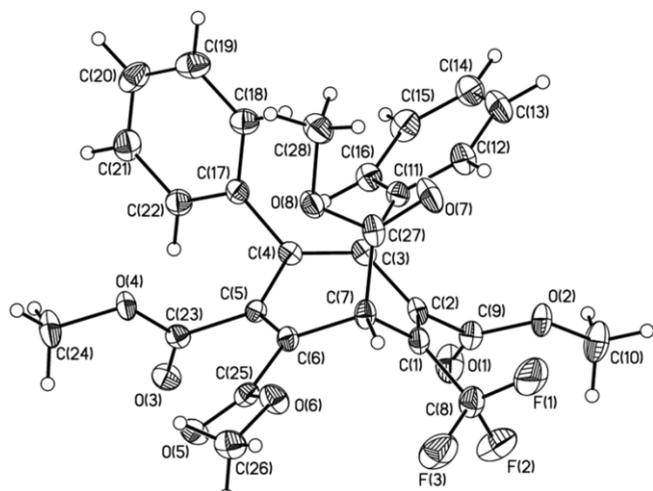
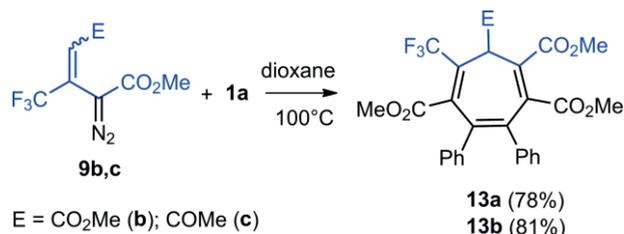


Figure 2. ORTEP-drawings for cycloheptatriene **13a**.

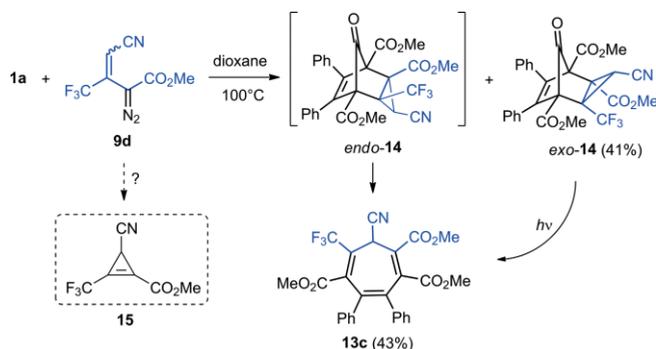
The results obtained prompted us to undertake a more detailed study of reactions of substituted vinyl diazoacetates with cyclopentadienones, **1a** in particular. To do so, acetyl- and cyano-substituted vinyl diazoacetates **9c,d** were also obtained by analogy with the synthesis of **9b**.^[8] It was found that the reaction of **1a** with **9c** in xylene heated at reflux gave an insuffi-

ciently high yield of the corresponding cycloheptatriene, which required an optimization of the reaction conditions. As it turned out, much better results were obtained when the reaction was carried out in dioxane under reflux conditions. In this case, not only the temperature decreased considerably, but also the reaction time decreased (from 8–10 h in xylene to 4 h in dioxane). In fact, the reaction of **1a** with diazo compounds **9b,c** in dioxane heated to reflux gave cycloheptatrienes **13a,b** in 78 and 81 % yields, respectively (Scheme 5). It should be noted that the use of $\text{Rh}_2(\text{OAc})_4$ in this process significantly reduced the yield of cycloheptatriene **13a** (up to 35 %), which indicates the noncarbene path of its formation.



Scheme 5. Reaction of diazo compounds **9b,c** with cyclopentadienone **1a** in dioxane at reflux.

An interesting result was obtained in the reaction of cyclopentadienone **1a** with cyano-substituted vinyl diazoacetate **9d**. In this case, along with cycloheptatriene **13c**, approximately the same amount of heptasubstituted tricyclo[3.2.1.0^{2,4}]oct-6-en-8-one, *exo*-**14**, was isolated (Scheme 6). The structures of these compounds were confirmed by X-ray single-crystal analysis (Figure 3).



Scheme 6. Reaction of diazo compound **9d** with cyclopentadienone **1a**.

Furthermore, we have shown that photolysis of *exo*-**14** in dioxane at 25 °C is accompanied by its decarbonylation to give the same cycloheptatriene **13c**. Based on these data, it can be assumed that the formation of the other cycloheptatrienes **13a–c** also occur through intermediate generation of tricyclic adducts **14** (Figure 4). However, the latter are probably formed as less thermally stable *endo* isomers (Scheme 6).

Thus, the formation of substituted cycloheptatrienes **13** in the reactions of cyclopentadienone **1** with vinyl diazoacetates **9** formally matches the [4+2]-cycloaddition of a diene to cyclopropene **15**. However, taking into consideration that cyclopentadienone **1** does not react with cyclopropene **8**, it is unlikely that similar reactions would occur with other cyclopropenes

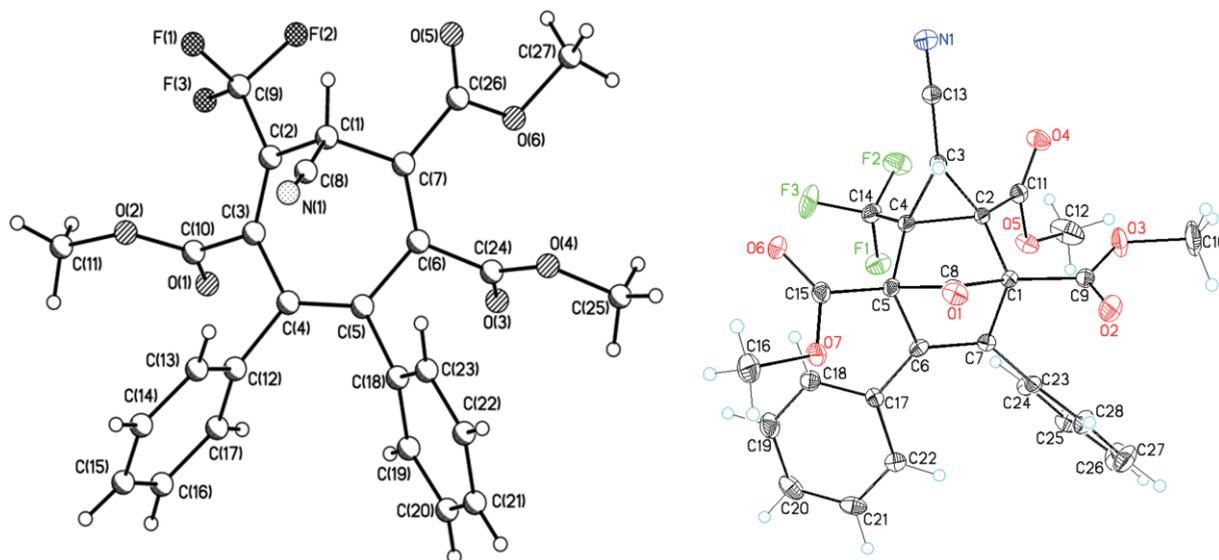


Figure 3. ORTEP-drawings for cycloheptatriene **13c** (left) and tricyclic compound **exo-14** (right).

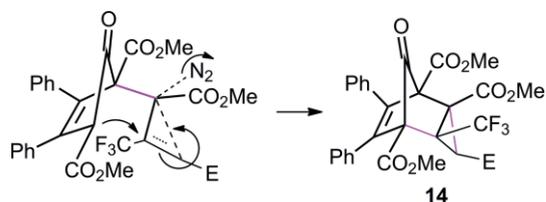
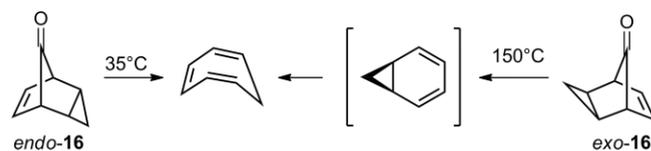


Figure 4. Possible transition state during the formation of the tricyclic structure.

containing three electron-withdrawing substituents in a molecule. Most likely, the reaction actually starts with formation of a C–C bond between the most reactive α -carbon atom of the diazo compound and the C(1) atom of the cycloidiene. Furthermore, a nitrogen-containing molecule is eliminated with simultaneous rearrangement of the carbon moiety, which results in the formation of two new C–C bonds; that is, formation of a three-membered ring and a norbornene structure. Apparently, in this case, the state in which the terminal end of the vinyl group in the diazo compound is remote from the carbonyl group of the cyclopentadienone is preferable and eventually results in a tricyclic structure with *endo*-orientation of the three-membered ring.

The ease of decarbonylation in the case of *endo*-isomers is in good agreement with the regularities of decarbonylation of isomeric tricyclo[3.2.1.0^{2,4}]oct-6-en-8-ones (**16**).^[9] In fact, the *endo*-isomer is readily decarbonylated even at 35 °C, whereas *exo-16* loses a CO molecule at the same rate only at 150 °C (Scheme 7).



Scheme 7. Conditions for the CO elimination from *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-8-ones.

Conclusions

We have suggested two regioselective methods for the synthesis of heptasubstituted cycloheptatrienes with several electron-withdrawing substituents in the ring. One of the methods involves the reaction of dialkyl 2-oxo-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylates **1** with cyclopropenes containing no electron-withdrawing substituents at the double bond. The second method, which is fundamentally new, involves the reaction of cyclopentadienones **1** with vinyl diazoacetates that, unlike cyclopropenes, should contain electron-withdrawing substituents at each carbon atom. In the latter case, the resulting cycloheptatrienes contain five electron-withdrawing substituents in the ring.

Experimental Section

General: ¹H and ¹³C NMR spectra were recorded with a 300 and 75.5 MHz NMR spectrometer for solutions in CDCl₃ containing 0.05 % of Me₄Si as an internal standard. ¹⁹F NMR spectra were recorded with a 188.3 MHz instrument and δ_f values are quoted relative to CCl₃F. Assignment of signals and determination of the structure compounds formed were made using COSY, HMBC, HSQC correlation spectra. High-resolution mass spectra were obtained with a Bruker micrOTOF II instrument (ESI, positive or negative ion modes, capillary voltage 4500 V). All chemical reagents and solvents were purchased from commercial sources and used without additional purification.

X-ray Diffraction Experiments were carried out with a SMART APEX II CCD diffractometer, using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å, ω -scans) at 120 K. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in the riding model. All calculations were performed by using SHELX-97 and SHELX-2014 software.^[10]

CCDC 1475655 (for **3a**), 1475656 (for **5**), 1475657 (for **6**), 1475658 (for **13a**), 1475659 (for **13c**), and 1475660 (for **exo-14**) contain the

supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Trimethyl 2,4-Dimethyl-6,7-diphenylcyclohepta-1,3,6-triene-1,3,5-tricarboxylate (3a): A solution of cyclopentadienone **1a** (1.84 g, 5.3 mmol) and cyclopropene **2a** (1.0 g, 8 mmol) was heated to reflux in xylene (8 mL) for 16 h. The solvent was evaporated in vacuo, the oily residue was dissolved in methanol (4 mL) and the solution was left to stand overnight at 0 °C. The precipitate was filtered and washed with a mixture of petroleum and diethyl ether (1:1) to give **3a** (1.77 g, 78 %) as a white solid; m.p. 151–153 °C. IR (KBr): $\tilde{\nu}$ = 2982, 2952, 1736, 1712, 1444, 1249, 1231, 1220, 1189, 1080, 1047, 1020, 702 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.13 (s, 5 H), 7.04–7.08 (m, 3 H), 6.96–7.01 (m, 2 H), 4.19 (s, 1 H), 3.84 (s, 3 H), 3.67 (s, 3 H), 3.29 (s, 3 H), 2.08 (s, 3 H), 1.99 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 170.5, 168.6, 168.2, 141.2, 140.8, 139.8, 138.5, 135.8, 135.1, 131.1, 129.9, 129.7, 128.1, 127.4, 127.3, 127.0, 57.8, 52.3, 52.0, 51.5, 23.2, 19.5 ppm. HRMS (ESI⁺): *m/z* calcd. for C₂₇H₂₆O₆Na⁺ [M + Na]⁺ 469.1627; found 469.1622.

Tetramethyl 6,7-Diphenyl-4-(trifluoromethyl)cyclohepta-1,4,6-triene-1,2,3,5-tetracarboxylate (13a): A solution of cyclopentadienone **1a** (1.15 g, 3.3 mmol) and diazo compound **9a** (1.0 g, 3.9 mmol) in dioxane (20 mL) was heated to reflux for 9.5 h. A new portion of **9a** (0.17 g, 0.7 mmol) was then added and the reaction mixture was additionally heated to reflux until the disappearance of the orange color, which is typical for cyclopentadienone **1a** (about 2 h). The solvent was evaporated by using a rotary evaporator, the residue was dissolved in methanol (4 mL) and the formed solution was left to stand overnight at 0 °C. The precipitate was filtered and washed with a mixture of petroleum and diethyl ether (1:1) to give **13a** (1.40 g, 78 %) as colorless crystals; m.p. 154–156 °C. IR (KBr): $\tilde{\nu}$ = 2958, 1736, 1724, 1434, 1277, 1253, 1181, 1169, 1125, 1097, 702 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.10–6.91 (m, 10 H), 5.16 (s, 1 H), 3.85 (s, 6 H), 3.46 (s, 3 H), 3.44 (s, 3 H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 168.9, 166.4, 165.1, 163.8, 143.3, 142.7, 141.9, 136.0, 130.0, 127.8, 125.1, 121.5 (q, ¹J_{C,F} = 274.5 Hz), 123.9 (q, ²J_{C,F} = 37.5 Hz), 53.4, 53.3, 52.6, 52.4, 41.4 ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ = –63.60 ppm. HRMS (ESI⁺): *m/z* calcd. for C₂₈H₂₃F₃O₈Na⁺ [M + Na]⁺ 567.1243; found 567.1228.

Reaction of Cyclopentadienone 1a with Diazobutenoate 9c: A solution of cyclopentadienone **1a** (1.19 g, 3.4 mmol) and diazo compound **9c** (0.90 g, 4.1 mmol) in dioxane (18 mL) was heated to reflux for 6 h. The solvent was evaporated by using a rotary evaporator, and the residue was separated by chromatography on silica gel (CHCl₃/EtOAc, 20:1) to give cycloheptatriene **13c** (0.75 g, 43 %) and tricyclo[3.2.1.0^{2,4}]octene **exo-14** (0.75 g, 41 %).

Trimethyl 7-Cyano-3,4-diphenyl-6-(trifluoromethyl)cyclohepta-1,3,5-triene-1,2,5-tricarboxylate (13c): Colorless crystals; m.p. 165 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2956, 1737, 1725, 1632, 1619, 1491, 1437, 1281, 1242, 1230, 1188, 1127, 1085, 765, 702 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.05–7.17 (m, 10 H), 5.44 (s, 1 H), 3.87 (s, 3 H), 3.49 (s, 3 H), 3.43 (s, 3 H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 165.4, 164.1, 162.2, 144.3, 143.7, 143.2, 138.7, 135.4, 135.5, 129.7, 128.2, 127.8, 120.8 (q, ¹J_{C,F} = 277.5 Hz), 120.4, 115.3, 53.8, 52.9, 52.7, 26.8 ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ = –63.31 ppm. HRMS

(ESI⁺): *m/z* calcd. for C₂₇H₂₀F₃NO₆Na⁺ [M + Na]⁺ 534.1140; found 534.1135.

exo-Trimethyl 3-Cyano-8-oxo-6,7-diphenyl-4-(trifluoromethyl)-tricyclo[3.2.1.0^{2,4}]oct-6-ene-1,2,5-tricarboxylate (exo-14): Colorless crystals; m.p. 185–187 °C. IR (KBr): $\tilde{\nu}$ = 3029, 2959, 2255, 1826, 1763, 1742, 1439, 1315, 1276, 1221, 1171, 996, 978, 702 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.40–7.00 (m, 10 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.72 (s, 3 H), 2.80 (s, 1 H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ = 175.8, 163.6, 163.1, 162.6, 144.6, 141.7, 132.4, 131.7, 130.1, 128.7, 128.1, 122.5 (q, ¹J_{C,F} = 277.9 Hz), 111.6, 71.8, 70.3, 53.5, 53.3, 53.2, 46.0 (q, ²J_{C,F} = 36.1 Hz), 45.1, 19.4 ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ = –59.23 ppm. HRMS (ESI⁺): *m/z* calcd. for C₂₈H₂₀F₃NO₇Na⁺ [M + Na]⁺ 562.1090; found 562.1084.

Supporting Information (see footnote on the first page of this article): All experimental details can be found in the supporting information. This includes experimental procedures, characterization data, and copies of ¹H, ¹³C and ¹⁹F NMR spectra.

Acknowledgments

High-resolution mass spectra were recorded in the Department of Structural Studies of the Zelinsky Institute of Organic Chemistry, Moscow.

Keywords: Small ring systems · Medium-ring compounds · Diazo compounds · Domino reactions · Cycloaddition

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Synthesis of Carbocycles

D. N. Platonov, A. Yu. Belyy,
I. V. Ananyev, Yu. V. Tomilov* 1–7



Synthesis of 1,2,3,4,5,6,7-Heptasubstituted Cycloheptatrienes through Cycloaddition Reactions of Substituted Cyclopentadienones



Regioselective convergent three- to four-step synthesis of heptasubstituted cycloheptatrienes with a wide range of substituents on the cycle was carried out, starting from 2-oxo-4,5-

diphenylcyclopenta-3,5-diene-1,3-dicarboxylate and 2,3-dimethyl(2,3-diphenyl)cycloprop-2-ene-1-carboxylates or 2-diazo-3-(trifluoromethyl)butenoates.

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