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Synthesis and properties of stable 1,2,3,4,5,6,7-heptamethoxycarbonyl cyclohepta-2,4,6-trien-1-yl potassium and its reactions with electrophilic reagents

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ABSTRACT

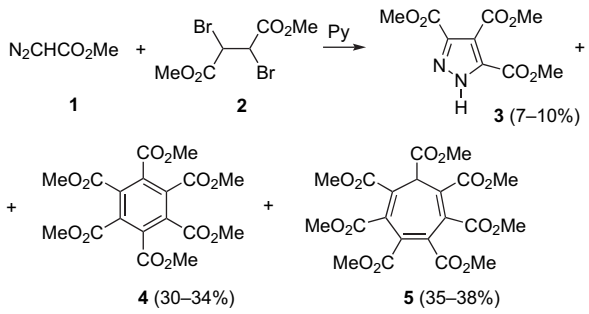
A new original one-pot procedure for the synthesis of a heptaester substituted cycloheptatriene from simple starting compounds, alkyl diazoacetate and 2,3-dibromosuccinate in pyridine was discovered. This compound, upon action of base, easily gives rise to the corresponding cycloheptatrienyl anion, which can be isolated as a stable salt. NMR and X-ray data of the compounds obtained are given. Reactions of this anion with electrophiles (methyl iodide, allyl bromide and diazonium salts) were also studied. In the last case, the 3a,7a-dihydroindazole derivatives were obtained as isolated products.

1. Introduction

Previously,[1,2] we have shown that diazoesters and diazoketones are able to react with some pyridinium ylides forming a covalent bond between the ylide carbon atom and the terminal nitrogen atom. Diazadiene obtained initially after the elimination of pyridine reacts with a pyridinium ylide with addition of one or two ylide fragments to the carbon atoms of C=N bonds connected to one electron-withdrawing group. The conversion level is defined by the nature of the functional groups and by the presence of substituents at the ylide carbon atom, and is completed, as a rule, by the formation of azaheterocycles—pyrazole, pyridazine or tetrahydropiridazine derivatives.[1–3] The initial interaction of the diazocarbonyl compound with the pyridinium ylide followed by the elimination of pyridine did not stop at the stage of azine formation, and the latter reacted easily with one more ylide molecules. This prompted us to study the behaviour of compounds able to generate two ylide centres in a molecule. As the starting material for this purpose we used dimethyl dibromosuccinate.

2. Results and discussion

In the present work, we studied the interaction of methyl diazoacetate (**1**) with dimethyl dibromosuccinate (**2**) in pyridine. A reaction mixture containing a threefold molar excess of *meso*-dibromosuccinate (**2**) was stirred for 48–60 h at room temperature until starting dibromide disappeared. During this period, the reaction mixture became practically black and pyridinium hydrobromide was partially precipitated. Most of pyridine was removed in vacuo and 3,4,5-trimethoxycarbonylpyrazole (**3**), benzenehexacarboxylic acid hexamethylester (**4**) and previously unknown cyclohepta-1,3,5-trieneheptacarbonic acid heptamethyl ester (**5**) were isolated by column chromatography on SiO_2, yield of the latter being up to 38% (Scheme 1).



Scheme 1.

The structure of cycloheptatriene **5** and the positions of the substituents were established from the X-ray analysis data (Table 1) of crystals isolated from the EtOAc solution upon gradual partial replacement of the solvent by THF, and from ^{1}H and ^{13}C NMR spectra.

Partial formation of the pyrazole **3** (7–10%) is likely to occur as a result of 1,3-dipolar addition of diazoacetate **1** to dimethyl

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Table 1
Key geometrical parameters of the molecules **5** and **7**

Bond	*d*/nm		Angle	*ω*/degree		Torsional angle	*ω*/degree	
	5	**7**		**5**	**7**		**5**	**7**
a	0.1496	0.1434	*ag*	104.8	127.5	*gab*	−72.1	−33.5
b	0.1337	0.1365	*ab*	122.2	119.3	*abc*	7.8	−28.5
c	0.1464	0.1490	*bc*	122.8	124.2	*bcd*	38.2	58.7
d	0.1358	0.1337	*cd*	123.3	120.3	*cde*	−2.2	−7.4
e	0.1462	0.1486	*de*	124.9	123.4	*def*	−40.0	−43.7
f	0.1338	0.1379	*ef*	123.5	122.1	*efg*	1.3	19.6
g	0.1511	0.1436	*fg*	121.4	121.3	*fga*	65.3	38.1

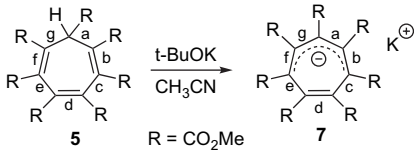
bromomaleate (**6**). The latter is formed as the main isomer by dehydrobromination of the initial dibromosuccinate **2** upon the action of pyridine, similarly to the action of triethylamine[4] (the chemical shift for olefinic proton of bromomaleate **6** is observed at δ_H 6.50 ppm, see lit.[5]). Trimethyl 2-pyrazolinetricarboxylate formed in the process easily loses HBr giving pyrazole **3**.

The formation of the cyclic products **4** and **5** is more complicated. The most likely rationale of their formation could be a cascade process involving three molecules of dimethyl 2-butynedioate (DMAD). This compound is known to be able to give benzenehexacarboxylate **4** in the presence of metal complex catalysts, for instance, cobalt compounds,[6] and to enter into successive reactions with active CH-acids in the presence of pyridine leading to linear or carbocyclic adducts constructed with participation of two or three molecules of DMAD.[7,8] But, firstly, the formation of this compound under the mild reaction conditions used is difficult to imagine and, secondly, we have shown that compounds **4** and **5** were not found in the reaction mixture while using DMAD instead of dibromosuccinate **2**.

Moreover, DMAD is known[9,10] to give 1,2,3,4-tetramethoxycarbonyl-9a*H*-quinolizine, formed from one molecule of pyridine and two molecules of DMAD, upon the action of pyridine. In our reaction of dibromide **2** with pyridine, we failed to detect a similar quinolizine. Thus, with the possibility of participation of DMAD in the formation of the carbocyclic compounds **4** and **5** being excluded, it should be accepted that the generation of the ylide-like molecule from the mono salt of dibromosuccinate **2** and pyridine is possible along with the formation of bromomaleate **6**. An intermediate formed either reacts then successively with two molecules of bromomaleate **6** with HBr elimination and further cyclization to give the stable compound **4**, or initially reacts with methyl diazoacetate and then according to the same scheme forms compound **5** (Scheme 2). At the present time the study of the mechanistic aspects of the reaction is under way.

The presence of the acceptor substituents in cycloheptatriene **5** implies its easy deprotonation upon action of base, resulting in generation of a cycloheptatrienyl anion.[11] In fact, the addition of 2 equiv of 1,4-diazabicyclo[2.2.2]octane (DABCO) to a solution of compound **5** in DMSO-d_6 results in a transformation in the four signals of the methoxy groups (δ 3.58, 3.75, 3.76 and 3.79 ppm, ratio 1:2:2:2) of the initial compound **5** into one singlet at δ 3.5 ppm in about 90%. In turn, acidification of the solution with CF_3CO_2H converts this ionized form to a neutral so that the spectrum of the initial compound **5** is recorded.

Stronger bases proved to be able both to shift the equilibrium towards the ionized form and to allow isolation of an individual salt-like compound. Thus, upon the action of potassium *tert*-butoxide in acetonitrile, a colourless solution of **5** became deep-crimson; after removal of the solvent and washing with THF the stable hepta(methoxycarbonyl)cyclohepta-2,4,6-trien-1-yl potassium (**7**) was obtained as deep-violet crystals (Scheme 3).



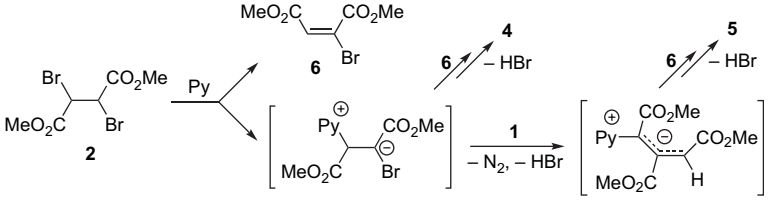
Scheme 3.

The structure of cycloheptatrienyl potassium **7** (Fig. 1) was established from X-ray analysis data. Comparison of bond lengths and angles in the neutral molecule **5** and anion **7** testifies that, in the anion, certain flattening of the seven-membered ring in relation to the *fgab* fragment and elongation of double and shortening of ordinary bonds adjacent to anion centre takes place (Table 1). This is indicative of partial conjugation involving the five carbon atoms of the carbocycle with delocalization of the negative charge on the oxygen atoms of the ester groups. At the same time the fragment *cde* is not included into the conjugated system, as pointed by the bond length C(4)═C(5) being close to that of the isolated double bond.

In the ^{1}H NMR spectra, the methoxy groups appear as a singlet at δ 3.48 ppm. In the ^{13}C NMR spectrum, only three signals are observed, thus confirming the equivalence of the seven-membered ring carbon atoms and of all seven ester groups. The spectrum remains the same when the sample is cooled down to −40 °C, evidence of fast dynamic processes in the solution.

Further, we have studied the alkylation of compound **7** with methyl iodide and allyl bromide. It was shown that, in both cases, the reaction in acetonitrile required heating of the reaction mixture for 24–30 h at reflux to reach completion. While the reaction with methyl iodide gave the anticipated product **8** in high yield, the reaction with allyl bromide did not stop at the stage of the allyl-derivative cycloheptatriene. The reaction product isolated in 65% yield is the tetracyclodecene derivative **9**, formed, apparently, as a result of an intramolecular rearrangement of the primary O-allylation product (Scheme 4). The C-allylation product does not obtain in this process (see below, compound **16**). If the same reaction is carried out at 30 °C for 5 days, the norcaradiene derivative **10** can be isolated as intermediate product. Heating leads to a [4+2]-cyclization of **10** into **9**, confirming *syn*-orientation of allyl substituent in **10**.

Further, we have studied the azocoupling reaction of the cycloheptatrienyl anion with diazonium salts using both classical aromatic diazo compounds, and the cyclopropyldiazonium ion generated in situ. Reactions with stable aryldiazonium salts **11a–c** were performed with compounds obtained by a standard technique—nitrosylation of the corresponding arylamine with sodium



Scheme 2.

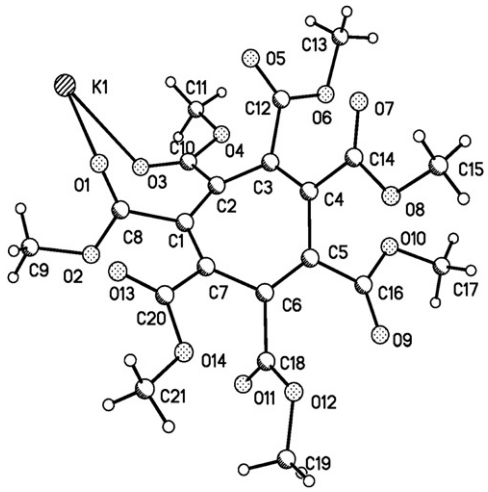
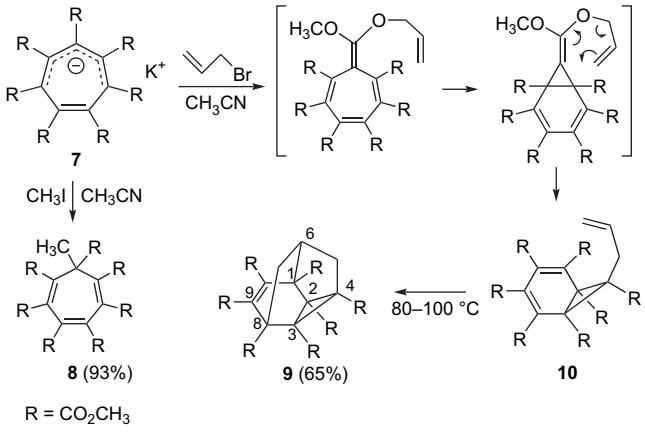
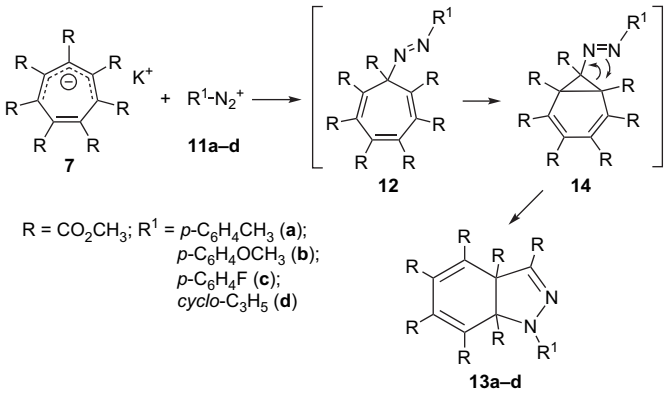


Figure 1. X-ray structure of molecule **7**.



Scheme 4.



Scheme 5.

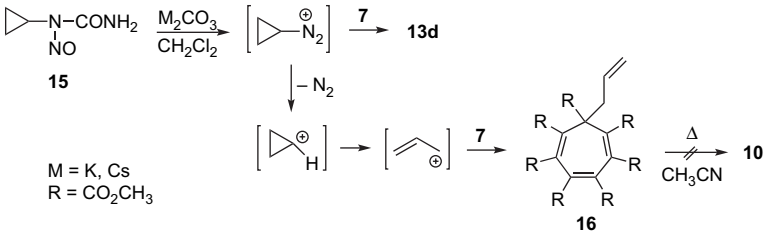
nitrite in the presence of hydrochloric acid. The reaction mixture was neutralized to pH=6, methylene chloride and cycloheptatrienyl potassium **7** were added at 5–20 °C. A standard workup gave crystalline compounds, elementary analysis data of which corresponded to the expected azocoupling adducts. However, ^{1}H and ^{13}C NMR spectra of the obtained compounds have shown that these were not azocycloheptatrienes **12** but rather 3a,7a-dihydroindazole derivatives **13a–c**. Apparently at the first step, as it was expected, the azocoupling of **7** with aryldiazonium ions **11a–c** did take place, but the resulting azocompounds **12**, having the possibility of the seven-membered ring contraction, are transformed initially into 7-azanorcaradienes **14**, which in turn easily isomerize into 3a,7a-dihydroindazoles **13a–c** (Scheme 5). These transformations are quite efficient and the yields of dihydroindazoles vary from 76 to 80%. Here we would like to point out the readiness of the isomerization of the azocyclopropane fragment into a condensed pyrazoline moiety. As it follows from the reaction conditions, this transformation proceeds at 5–20 °C already, which is apparently due to the presence of the electron acceptor substituents in the cyclopropane ring. Azacyclopropane isomerization examples described earlier involved thermal or photochemical interactions.[12,13]

The successful formation of dihydroindazoles is evidence of the high rate of the initial azocoupling reaction, this rate being greater than that of the cycloheptatrienyl sodium hydrolysis, which allows aqueous diazonium salt solutions in this process. It is interesting to note that the nature of the diazonium salt aromatic ring substituents has little effect on the azocoupling reaction, but its efficiency is notably susceptible to the pH of the reaction medium. Maximum yields of the target dihydroindazoles are achieved at pH about 6.0.

A similar reaction is observed at a generation of cyclopropyldiazonium ion (**11d**), which is known[14,15] to couple with active azo components and CH-acids giving cyclopropylazoarenes and *N*-cyclopropylhydrazones. The cyclopropyldiazonium ion generated upon the decomposition of *N*-cyclopropyl-*N*-nitrosourea (**15**) with potassium or cesium carbonate at 3–6 °C readily reacts with the anion **7**. The optimal reaction conditions were found to be the generation of the cycloheptatrienyl anion and diazonium ion **11d** by a successive addition of compound **5**, cesium carbonate and nitrosourea **15** in a molar ratio of 1:3:1.5. Similarly, to the aryldiazonium salts, the isolable product of this reaction is a 3a,7a-dihydroindazole derivative **13d** (Scheme 5), the yield of which in these conditions is 80–83%. The structure of **13d** was established by an X-ray of a single crystal obtained by crystallization from benzene–petroleum ether.

Along with dihydroindazole **13d**, we have also isolated 7-allylcyclohepta-1,3,5-trieneheptacarboxylate **16** with a yield of 10–12%. The formation of allylic derivatives in the conditions of cyclopropyldiazonium generation is quite a typical process, and this reaction is more or less observable in virtually every cyclopropyldiazonium transformation due to its tendency towards dediazotation with subsequent isomerization of the formed cyclopropyl cation into a stable allylic cation[15,16] (Scheme 6). The allylic derivative **16**, which was isolated by column chromatography using silica gel, was found to be quite stable, and in contrast to the allyl bromide alkylation product of **7** does not convert into the norcaradiene **10** or into the tetracyclodecene derivative **9** upon being heated in acetonitrile. This result shows that the alkylation of the cycloheptatrienyl anion with allyl bromide and the allyl cation generated by the dediazotation of the diazonium ion involves different mechanisms. The latter case apparently involves a usual ion pair recombination, which leads to the C-alkylation product, which is stable under the given conditions and does not isomerize into norcaradieneheptacarboxylate **10**.

The reaction of compound **7** with allyl bromide is a nucleophilic substitution and it is affected by a number of factors, including electronic and steric ones. These factors seem to govern the initial formation of the O-alkylation product, which undergoes an intramolecular allylic rearrangement simultaneously with a cycloheptatriene–norcaradiene isomerization. It should be noted that norcaradiene **10** was found to be quite stable, in contrast to, e.g., the majority of [1+2]-cycloadducts of carbonylcarbenes with benzene



Scheme 6.

and its derivatives.[17] Nevertheless there is an example of a stable ethyl 3,4-dimethoxynorcaradiene-7-carboxylate, which isomerized into the corresponding cycloheptatriene upon heating above 100 °C.[18] In our report, the norcaradiene **9** overloaded by electron acceptor substituents did not isomerize upon heating into the cycloheptatriene **16**, but gave the tetracyclic compound **9** (Scheme 4) via an intramolecular, inverse electron demand Diels–Alder reaction.

In summary, we have found a new one-pot route to synthesize a heptaester of a substituted cycloheptatriene (**5**) from three molecules of dimethyl 2,3-dibromosuccinate and one molecule of methyl diazoacetate in pyridine. Compound **5** easily forms the corresponding cycloheptatrienyl anion, such as 1,2,3,4,5,6,7-(heptamethoxycarbonyl)cyclohepta-2,4,6-trien-1-yl potassium (**7**), stable in common conditions. This anion reacts with electrophiles, while the presence of multiple bonds in the side chains of the products leads to further intramolecular transformations, allowing synthesis of caged or heterocyclic compounds.

3. Experimental section

3.1. General

All reagents and solvents used were commercial grade chemicals. *N*-Cyclopropyl-*N*-nitrosourea (**15**) was prepared by a known procedure.[16,19] The TLC analysis was performed on Silufol chromatographic plates (Merck). For preparative chromatography, silica gel 60 (0.040–0.063 mm; Merck) was used. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75 MHz, respectively) in $CDCl_3$ or $(CD_3)_2SO$ both containing 0.05% Me_4Si as the internal standard. The ^{19}F NMR spectrum was recorded on a Bruker AC-200 (188.3 MHz) instrument and δ_F values are quoted relative to CCl_3F. IR spectra were obtained using a Specord M80-2 spectrometer as potassium bromide disks. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet probe). The elemental compositions were determined on a Perkin–Elmer Series II 2400 CHN Analyzer.

*3.1.1. Cyclohepta-1,3,5-triene-1,2,3,4,5,6,7-heptacarboxylic acid heptamethyl ester (**5**)*

A solution of dimethyl 1,2-dibromosuccinate (**1**, 3.65 g, 12.0 mmol) and methyl diazoacetate (**2**, 0.40 g, 4.0 mmol) in pyridine (20 mL) was stirred for 48–60 h at 20 °C until starting dibromide **1** disappeared. Pyridine was removed in vacuo and 0.15 M aqueous $NaHSO_4$ (35 mL) was added to the black residue. The reaction mixture was extracted with ethyl acetate (2×30 mL) and the organic layer was dried over Na_2SO_4. The solvent was removed in vacuo and the mixture was separated by column chromatography on silica gel (benzene–EtOAc, 1:1) to afford compound **5**: 35–38%; colourless crystals, mp 136–137 °C; ν (cm^{-1}) 1760, 1750 and 1726 (C=O), 1612 and 1600 (C=C), 1458, 1435; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (s, 3H, OCH_3), 3.75, 3.76, 3.79 (all s, 3×6H, 6OCH_3), 5.13 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.4 (CH), 53.0, 53.3, 53.4 (3×2OCH_3), 53.1 (OCH_3), 132.2, 133.7, 136.8 (3×2C), 164.0, 164.5, 166.8 (3×2COO), 164.6 (COO); EIMS (*m*/*z*, relative intensity): 467 [(M−OCH_3)$^+$, 28], 439 [(M−CO_2CH_3)$^+$, 100]. Anal. calcd for $C_{21}H_{22}O_{14}$: C, 50.61; H, 4.45. Found: C, 50.47; H 4.78.

*3.1.2. 1,2,3,4,5,6,7-Heptamethoxycarbonylcyclohepta-2,4,6-trien-1-yl potassium (**7**)*

Potassium *tert*-butoxide (0.16 g, 1.4 mmol) was added to a solution of compound **5** (0.70 g, 1.4 mmol) in acetonitrile (15 mL) and stirred for 1 h at 20 °C. The solvent was removed in vacuo and the residue was washed with THF (10 mL) to afford compound **7** (0.68 g, 90%) as crimson crystals, mp 252–257 °C; ν (cm^{-1}) 1760, 1748 and 1724 (C=O), 1636 and 1564 (C=C), 1460, 1432; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.48 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.3 (OCH_3), 132.4 (C), 166.8 (COO). Anal. calcd for $C_{21}H_{21}KO_{14}$: C, 47.02; H, 3.95. Found: C, 46,61; H, 4.02.

*3.1.3. 7-Methyl-1,2,3,4,5,6,7-(heptamethoxycarbonyl)cyclohepta-1,3,5-triene (**8**)*

Methyl iodide (0.57 g, 4 mmol) was added to a solution of compound **7** (0.54 g, 1 mmol) in acetonitrile (10 mL) and the mixture was heated at reflux until disappearance of the colour (approximately 24 h). The solvent was removed in vacuo and the residue was purified by passing through a layer of silica gel (approx. 5 cm^3) eluted by mixture of benzene–EtOAc, 1:1 to afford compound **8** (0.475 g, 93%) as colourless crystals, mp 145–146 °C; ν (cm^{-1}) 1756, 1740 and 1724 (C=O), 1620 (C=C), 1460, 1440; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (s, 3H, CH_3), 3.61 (s, 3H, OCH_3), 3.74, 3.79 and 3.83 (all s, 3×6H, 6OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7 (CH_3), 48.8 (C), 52.8, 53.1, 53.1 (3×2OCH_3), 53.7 (OCH_3), 128.2, 135.9, 141.9 (3×2C), 164.2, 164.5, 164.9 (3×2CO), 170.4 (CO); EIMS (*m*/*z*, relative intensity): 453 [(M−CO_2CH_3)$^+$, 3], 59 [100]. Anal. calcd for $C_{22}H_{24}O_{14}$: C, 51.57; H, 4.72. Found: C, 51.33; H 4.79.

*3.1.4. 1,2,3,4,8,9,10-Hepta(methoxycarbonyl)tetracyclo-[4.4.0.0^{2,4}.0^{3,8}]dec-9-ene (**9**)*

Allyl bromide (0.73 g, 6 mmol) was added to a solution of compound **7** (0.54 g, 1 mmol) in acetonitrile (10 mL) and the reaction mixture was heated at reflux until disappearance of the colour (approximately 30 h). The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (benzene–EtOAc, 1:1) to afford compound **9** (0.538 g, 65%) as colourless crystals, mp 182–183°C; ν (cm^{-1}) 1748 and 1736 (C=O), 1616 (C=C), 1453, 1436; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (dd, 1H, H(7a), ^2J=12.5 Hz, ^3J=8.0 Hz), 2.10 (d, 1H, H(7b), ^2J=12.5 Hz), 2.14 (d, 1H, H(5a), ^2J=12.5 Hz), 2.46 (dd, 1H, H(5b), ^2J=12.5 Hz, ^3J=5.0 Hz), 2.70 (dd, 1H, H(6), ^3J=8.0, 5.0 Hz), 3.62 (s, 3H, CO_2CH_3 at C(3)), 3.69 (s, 3H, CO_2CH_3 at C(2)), 3.70 (s, 3H, CO_2CH_3 at C(8)), 3.73 (s, 6H, 2CO_2CH_3 at C(1) and C(4)), 3.74 (s, 6H, 2CO_2CH_3 at C(9) and C(10)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.5 (C(6)), 36.4 (C(5)), 39.3 (C(7)), 45.4 (C(4)), 46.4 (C(3)), 51.4 (C(2)), 52.46, 52.52, 52.81, 52.85, 52.98 (7OCH_3), 53.8 (C(8)), 60.2 (C(1)), 135.2 (C(10)), 146.7 (C(9)), 163.9 and 165.9 (2COO at C(9) and C(10)), 165.5 (COO, C(2)), 165.9 (COO, C(3)), 167.0 (COO, C(4)), 169.7 (COO, C(8)), 170.2 (COO, C(1)); EIMS (*m*/*z*, relative intensity):539 [M$^+$, 6], 507 [(M−OCH_3)$^+$, 18], 447

[(M−$COOCH_3$)$^+$, 7], 59 [100]. Anal. calcd for $C_{24}H_{26}O_{14}$: C, 53.54; H, 4.87. Found: C, 53.36; H, 5.12.

*3.1.5. Identification of 7-allyl-1,2,3,4,5,6,7-hepta(methoxycarbonyl)bicyclo[4.1.0]hepta-2,4-diene (**10**) and its transformation to compound **9***

Allyl bromide (0.36 g, 3 mmol) was added to a solution of compound **7** (0.27 g, 0.5 mmol) in acetonitrile (5 mL) and the reaction mixture was stirred for 120 h at 30 °C. In these conditions, conversion of **7** was approximately 12–15%. Then the solvent was removed in vacuo and the residue was separated by column chromatography on silica gel (benzene–EtOAc, 1:1). A mixture of compound **10** and cycloheptatriene **5** in ratio 1.6:1 according to ^{1}H NMR spectrum was isolated: colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.05 (d, 2H, CH_2, J=7.0 Hz), 3.80, 3.84, 3.89 (all s, 3×6H, 6OCH_3), 3.81 (s, 3H, OCH_3), 5.00–5.19 (m, 2H, =CH_2), 5.71–5.96 (m, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.5 (C(1) and C(6)), 36.1 (CH_2), 39.4 (C(7)), 52.6, 52.9, 53.6 (3×2OCH_3), 53.4 (OCH_3), 119.2 (=CH_2), 119.6 (C(2) and C(5)), 128.4 (C(3) and C(4)), 132.4 (=CH), 164.5, 165.1, 167.7 (3×2COO), 165.2 (COO). Then the mixture obtained was refluxed in acetonitrile during 24 h and according to ^{1}H NMR spectrum compound **10** transformed completely to tetracyclodecene **9**.

3.2. Heptamethyl 1-aryl-3a,7a-dihydro-1*H*-indazole-3,3a,4,5,6,7,7a-heptacarboxylates (13a–c). General procedure

The arylamine (4 mmol) was added at 0–5 °C to a solution of concentrated hydrochloric acid (0.42 mL) and about of water (250 mg), and the mixture was stirred for 20 min. A cooled $NaNO_2$ (0.29 g, 4.2 mmol) solution in H_2O (0.7 mL) was added dropwise while the reaction temperature was maintained at about 2 °C and the mixture was stirred for 20 min. To the obtained diazonium salt $NaHCO_3$ was added in small portions until pH ~6, after that methylene chloride (2 mL) and cycloheptatrienyl potassium **7** (1.07 g, 2 mmol) were added. The reaction mixture was stirred for 2 h at 2–5 °C, allowed to warm to 20 °C, methylene chloride (2 mL) and water (1 mL) were added to facilitate separation, the organic layer was washed with water (2×3 mL), dried over anhydrous $MgSO_4$ and the solid residue after solvent removal was crystallized from EtOAc–petrol ether mixture (1:1).

*3.2.1. Heptamethyl 1-p-tolyl-3a,7a-dihydro-1H-indazole-3,3a,4,5,6,7,7a-heptacarboxylate (**13a**)*

Yield: 80%; yellow solid, mp 137–138 °C; ν (cm^{-1}) 1772, 1756, 1728 and 1720 (C=O), 1552 (C=C), 1512 (C=N), 1460, 1436; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H, CH_3), 3.39, 3.58, 3.77, 3.82 and 3.91 (all s, 5×3H, 5OCH_3), 3.81 (s, 6H, 2OCH_3), 7.10 and 7.30 (both d, 2×2H, 4CH, ^3J=8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2 (CH_3), 52.5, 52.6, 53.1, 53.2, 53.3, 53.4 and 54.1 (7OCH_3), 67.2 (C(3a)), 81.7 (C(7a)), 124.7 and 127.0 (C(4) and C(7)), 126.7 (2 *m*-C), 128.9 (2 *o*-C), 132.8 and 135.0 (C(5) and C(6)), 137.3 (*i*-C), 137.6 (*p*-C), 138.5 (C(3)), 161.6, 163.3, 163.9, 164.6, 164.7, 165.8 and 166.2 (7COO). Anal. calcd for $C_{28}H_{28}N_2O_{14}$: C, 54.55; H, 4.58; N, 4.54. Found C, 54.13; H, 4.82; N, 4.21.

*3.2.2. Heptamethyl 1-(4-methoxyphenyl)-3a,7a-dihydro-1H-indazole-3,3a,4,5,6,7,7a-heptacarboxylate (**13b**)*

Yield: 79%; orange solid, mp 173–174 °C; ν (cm^{-1}) 1768, 1752, 1732 and 1720 (C=O), 1552 (C=C), 1512 (C=N), 1462, 1440; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35, 3.55, 3.78, 3.80, 3.81, 3.82, 3.84 and 3.88 (all s, 8×3H, 8OCH_3), 6.82 (d, 2H, 2 *m*-CH, J=8.9 Hz), 7.37 (d, 2H, 2 *o*-CH, J=8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.5, 52.6, 53.1, 53.2, 53.3, 53.4, 54.1 and 55.4 (8OCH_3), 67.1 (C(3a)), 81.7 (C(7a)), 113.4 (2 *m*-C), 124.6 and 127.1 (C(4) and C(7)), 128.6 (2 *o*-C), 132.4 and 134.9 (C(5) and C(6)), 134.0 (*i*-C), 137.6 (C(3)), 158.8 (*p*-C), 161.6, 163.4, 163.9, 164.7, 164.8, 165.8 and 166.2 (7COO). Anal. calcd for $C_{28}H_{28}N_2O_{15}$: C, 53.17; H, 4.46; N, 4.43. Found: C, 52.78; H, 4.63; N, 4.09.

*3.2.3. Heptamethyl 1-(4-fluorophenyl)-3a,7a-dihydro-1H-indazole-3,3a,4,5,6,7,7a-heptacarboxylate (**13c**)*

Yield: 76%; yellow solid, mp 88–89 °C; ν (cm^{-1}) 1772, 1748, 1732 and 1724 (C=O), 1560 (C=C), 1508 (C=N), 1460, 1440; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.43, 3.59, 3.78, 3.80, 3.81, 3.83 and 3.88 (all s, 7×3H, 7OCH_3), 7.01 (dd, 2H, 2 *m*-CH, $J_{H,H}$=9.0 Hz, $J_{H,F}$=8.5 Hz), 7.45 (dd, 2H, 2 *o*-CH, $J_{H,H}$=9.0 Hz, $J_{H,F}$=5.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 52.7, 53.1, 53.2, 53.3, 53.5 and 54.1 (7OCH_3), 67.2 (C(3a)), 81.7 (C(7a)), 115.1 (d, *m*-C, $^2J_{H,F}$=22.5 Hz), 124.7 and 127.0 (C(4) and C(7)), 128.9 (d, *o*-C, $^3J_{H,F}$=9.0 Hz), 133.5 and 134.9 (C(5) and C(6)), 137.1 (d, *i*-C, $^4J_{H,F}$=3.0 Hz), 137.7 (C(3)), 161.6 (d, *p*-C, $J_{H,F}$=246 Hz), 161.4, 163.2, 163.9, 164.5, 164.6, 165.6 and 166.0 (7COO); ^{19}F NMR (282 MHz, $CDCl_3$), δ −114.5 (tt, J=8.5, 5.0 Hz). Anal. calcd for $C_{27}H_{25}FN_2O_{14}$: C, 52.26; H, 4.06; N, 4.51. Found: C, 52.20; H, 4.32; N, 4.19.

*3.2.4. 1-Cyclopropyl-3a,7a-dihydro-1H-indazole-3,3a,4,5,6,7,7a-heptacarboxylic acid heptamethyl ester (**13d**) and heptamethyl 7-allylcyclohepta-1,3,5-triene-1,2,3,4,5,6,7-heptacarboxylate (**16**)*

A mixture of ester **5** (1 g, 2 mmol) and Cs_2CO_3 (1.45 g, 7.5 mmol) in CH_2Cl_2 (50 mL) was stirred for 2 h at 5–7 °C, cyclopropylnitrosourea **15** (0.39 g, 3 mmol) was added in portions at that temperature and the mixture was stirred for 3 h. The reaction mixture was filtered through a thin layer of silica gel (~0.5 cm^3), the precipitate was washed with ethyl acetate and the solvent was removed in vacuo. The residue was crystallized twice from a benzene–petrol ether mixture, giving 0.90 g of **13d**: 80%; yellow crystals, mp 189–190 °C; ν (cm^{-1}) 1760, 1746 and 1732 (C=O), 1562 (C=C), 1518 (C=N), 1455, 1440; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56–0.66 and 0.87–1.04 (both m, 2×2H, CH_2CH_2), 3.17–3.26 (m, 1H, CH), 3.66, 3.74, 3.75, 3.77, 3.78, 3.80 and 3.84 (all s, 7×3H, 7OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.7 and 8.4 (CH_2CH_2), 31.3 (CH), 52.4, 52.8, 52.9, 53.0, 53.3, 53.5 and 53.8 (7OCH_3), 66.8 (C(3a)), 80.5(C(7a)), 125.7 and 126.5 (C(4) and C(7)), 131.3 and 133.3 (C(5) and C(6)), 136.8 (C(3a)), 161.3, 163.4, 164.6, 164.7, 164.8, 166.1 and 166.2 (7COO); EIMS (*m*/*z*, relative intensity): 507 [(M−CO_2CH_3)$^+$, 8], 395 [(C_6(CO_2CH_3)$_5$CO)$^+$, 48], 59 [(CO_2CH_3)$^+$, 100], 41 [$C_3H_5^+$, 75]. Anal. calcd for $C_{24}H_{26}N_2O_{14}$: C, 50.89; H, 4.63; N, 4.95. Found: C, 51.24; H, 4.98; N, 4.64.

Mother liquor after isolation of **13d** was concentrated and the residue was purified by column chromatography on silica gel (benzene–EtOAc, 1:1) to afford compound **16**: ~10%; colourless easily melted crystals; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.18 (dt, 2H, CH_2, ^3J=7.3 Hz, ^4J=1.1 Hz), 3.66 (s, 3H, CO_2CH_3 at C(7)), 3.82, 3.87 and 3.89 (all s, 3×6H, 6OCH_3), 4.97–5.04 (m, 2H, =CH_2), 5.38 (ddt, 1H, =CH, J_{trans}=17.1 Hz, J_{cis}=9.7 Hz, ^3J=7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.1 (CH_2), 67.5 (C(7)), 52.8, 52.9 and 53.6 (6OCH_3), 53.5 (OCH_3), 120.0 (=CH_2), 129.3 (=CH), 134.0, 141.2 and 143.1 (C=C in cycle), 162.1, 162.6 and 165.2 (6COO), 167.1 (COO at C(7)). Anal. calcd for $C_{24}H_{26}O_{14}$: C, 53.54; H, 4.87. Found: C, 53.68; H, 5.04.

4. Crystallographic material

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 683945 for cycloheptatrieneheptacarboxylate **5**, CCDC 683946 for cycloheptatrienyl potassium **7** and CCDC 683947 for dihydroindazole derivative **13d**. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road,

Cambridge, CB2 1EZ, UK (fax: +44 1223 33603 or e-mail: deposit@ccdc.cam.ac.uk).

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References and notes

1. Tomilov, Y. V.; Platonov, D. N.; Dorokhov, D. V.; Nefedov, O. M. *Russ. Chem. Bull., Int. Ed.* **2005**, *54*, 1008–1012.
2. Tomilov, Y. V.; Platonov, D. N.; Dorokhov, D. V.; Kostyuchenko, I. V. *Russ. Chem. Bull., Int. Ed.* **2006**, *55*, 112–117.
3. Tomilov, Y. V.; Platonov, D. N.; Dorokhov, D. V.; Nefedov, O. M. *Tetrahedron Lett.* **2007**, *48*, 883–886.
4. Huddleston, P. R.; Barker, J. M.; Stickland, B.; Wood, M. L.; Guindi, L. H. M. *J. Chem. Res., Miniprint* **1988**, *8*, 1871–1890.
5. Liard, J.-L.; Jasse, B.; Poisson, R. *Bull. Soc. Chim. Fr.* **1973**, 3006–3009.
6. Saino, N.; Amemiya, F.; Tanabe, E.; Kase, K.; Okamoto, S. *Org. Lett.* **2006**, *7*, 1439–1442.
7. Le Goff, E.; La Count, R. B. *J. Org. Chem.* **1964**, *29*, 423–427.
8. Diels, O. *Chem. Ber.* **1942**, *75*, 1452–1467.
9. Acheson, R. M.; Hole, F. *J. Chem. Soc.* **1962**, 748–752.
10. Bamfield, P.; Crabtree, A.; Johnson, A. W. *J. Chem. Soc.* **1965**, 4355–4362.
11. Cycloheptatrienyl anion formation was shown previously by physical methods in gas phase or in solution, in most cases were condensed structures having some double bonds in a molecule were investigated: (a) Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6499–6501; (b) Maas, W. P. M.; Veelen, P. A.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1989**, *24*, 546–558; (c) Tolbert, L. M.; Zaki Ali, M. *J. Org. Chem.* **1982**, *47*, 4793–4795; (d) Huning, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, *12*, 1959–1971.
12. (a) Engel, P. S.; Wu, W.-X. *J. Org. Chem.* **1990**, *55*, 1503–1505; (b) Engel, P. S.; Bodager, G. A. *J. Org. Chem.* **1986**, *51*, 4792–4796; (c) Engel, P. S.; Bodager, G. A. *J. Org. Chem.* **1988**, *53*, 4748–4758.
13. Rosenkranz, H. J.; Schmid, H. *Helv. Chim. Acta* **1968**, *51*, 1628–1631.
14. (a) Tomilov, Y. V.; Kostyuchenko, I. V.; Shulishov, E. V.; Nefedov, O. M. *Mendeleev Commun.* **2002**, 104–106; (b) Tomilov, Y. V.; Kostyuchenko, I. V.; Shulishov, E. V.; Okonnishnikova, G. P. *Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 993–997.
15. Klimenko, I. P.; Korolev, V. A.; Tomilov, Y. V.; Nefedov, O. M. *Russ. J. Org. Chem.* **2006**, *42*, 1299–1306.
16. Kirmse, W.; Schütte, H. *Chem. Ber.* **1968**, *101*, 1674–1688.
17. (a) Nefedov, O. M.; Shapiro, E. A.; Dyatkin, A. B. In *The Chemistry of Functional groups, Suppl B, The Chemistry of Acid Derivatives*; Patai, S., Ed.; J. Wiley & Sons: New York, US, 1992; Vol. 2, pp 1591–1595; (b) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds. From Cyclopropanes to Ylides*; J. Wiley & Sons: Guiford, UK, 1997; pp 289–354.
18. Matsumoto, M.; Shiono, T.; Mutoh, H.; Amano, M.; Arimitsu, S. *J. Chem. Soc., Chem. Commun.* **1995**, 101–102.
19. Gol'mov, V. P. *Zh. Obshch. Khim. (Russ.)* **1935**, *5*, 1562–1565; [*Chem. Zentralbl.* **1936**, *107*, 1905].