3,4-Diacetylhexane-2,5-dione — an effective synthon for synthesis of substituted azulene heteroanalogs by cyclocondensation reactions

E. P. Olekhnovich,[a] S. L. Boroshko,[b] Yu. N. Tkachenko,[b] A. F. Pozharskii,[b] E. B. Tsupak,[b] Yu. A. Zhdanov,[b] and L. P. Olekhnovich[b]*

[a]*Scientific-Research Institute of Physical and Organic Chemistry, Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. Fax: +7 (863 2) 28 5667*

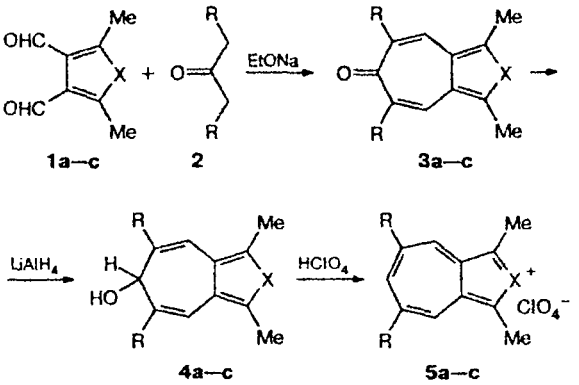
[b]*Department of Chemistry, Rostov State University, 7 ul. Zorge, 344090 Rostov-on-Don, Russian Federation. Fax: +7 (863 2) 64 5255. E-mail: root@chimfak.rnd.runnet.ru*

The one-pot method for the synthesis of 4,8-dialkoxy-6-aryl-1,3-dimethylcyclohepta[*c*]furanium perchlorates has been developed. The method is based on the cyclocondensation of 3,4-diacetylhexane-2,5-diones with aromatic aldehydes and trialkyl orthoformates under the action of a 16% perchloric acid solution in acetic anhydride. Under similar conditions, with hydrogen sulfide, cyclohepta[*c*]thiophenium perchlorates have been obtained, while cyclohepta[*c*]pyrrolium perchlorates have been prepared with arylamines, ammonium acetate, or aliphatic amine acetates. A heteroanalog of azulene, 4,8-diethoxy-1,3-dimethyl-2-azaazulene, has been obtained for the first time. Hydrolysis of aza- and thiaazulenium salts gives the corresponding cyclohepta[*c*]pyrrol-4-ones and cyclohepta[*c*]thiophen-4-ones.

Key words: 3,4-diacetylhexane-2,5-diones, ammonium acetate, primary amines, hydrogen sulfide, 3,4-diacetyl-1,3-dimethylpyrroles(-thiophenes, -furans), perchloric acid, triethyl orthoformate, cyclohepta[*c*]pyrrolium, -thiophenium, -furanium perchlorates, 4,8-diethoxy-1,3-dimethyl-2-azaazulene, 2-aryl-1,3,6-trimethylcyclopenta[*c*]pyrrol-4-one.

Search for methods of synthesis and study of properties of tropolones, their condensed analogs, azulenes and heteroazulenes, and the corresponding cations are a popular topic of research.[1,2] Representatives of azulenes possess antiphlogistic,[3] anticancer,[4] and bacteriostatic[5] properties and have valuable spectral parameters.[6] About 30 years ago,[7,8] the sequence of reactions (Scheme 1) for the development of azulene heteroanalogs of type **5a,b** was developed. A 2,5-dimethyl-substituted heterocycle (pyrrole or thiophene) is synthesized first, then it is formylated at free positions 3 and 4. Diformylpyrroles (thiophenes) (**1a,b**) are transformed into cyclohepta[*c*]pyrrol-6-ones and -thiophen-6-ones (**3a,b**) by the action of dimethylene ketones (**2**), and then **3a,b** are reduced to carbinols (**4a,b**). The latter are treated with hydrochloric acid to obtain cyclohepta[*c*]pyrrolium and -thiophenium perchlorates **5a,b**. Scheme 1 underwent no changes in subsequent synthetic works, and this method was successfully used for preparing cyclohepta[*c*]furylium cations (**5c**).[9] The method has some disadvantages, such as narrow limits of variation of the starting reagents and substrates, but no alternative ways for the synthesis of azulene heteroanalogs with the axial symmetry have not been proposed up to the recent years.

Scheme 1



a: X = N—Ar, **b**: X = S, **c**: X = O

We propose 3,4-diacetylhexane-2,5-dione (**6**) existing in the form of diketoenol as the main starting synthon.[10] It is well known that 1,4-diketones in the presence of acids are cyclized to furans[11] and react readily with hydrogen sulfide and amines[12,13] to form the corresponding thiophenes and pyrroles. Since

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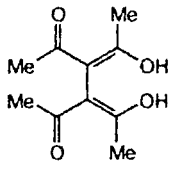
tetraketone **6** can be simultaneously considered as 1,3--and 1,4-diketone, it can form five-membered heterocycles (**7—9**) with acetyl groups in positions 3 and 4, which are convenient for annelation of the seven-membered cycle.

In fact, oxygen analogs of azulene, 1,3-dimethyl-4,8-dialkoxycyclohepta[*c*]furylium perchlorates (**10**, R^1 = Alk, R^2 = H), are formed in one-pot synthesis under mild conditions and in high yields by acid ($HClO_4$) cyclocondensation of tetraketone **6** with trialkyl orthoformates, whereas in the presence of aromatic aldehydes with electron-releasing substituents, a series of 6-aryl-substituted salts of cyclohepta[*c*]furylium (**10**, R^1 = Alk; R^2 = Ar) was obtained.[14] 2,5-Dimethyl-3,4-diacetylfuran (**7**) was formed as an intermediate and, in some cases, was isolated. Perchlorates of type **10**, unlike perchlorates **5a—c**, have reactive alkoxy groups in positions 4 and 8. Therefore, they are of interest as the starting compounds for synthesis of various arylamino- and hetarylamino-derivatives of cyclohepta[*c*]furan-4-ones and cyclohepta[*c*]furan-4-ol-8-ones.[15]



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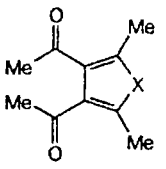
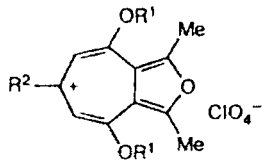


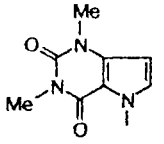
7—9



10

7: X = O; **8**: X = N—R; R = H (**a**), Me (**b**), 4-MeC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 2-$NH_2C_6H_4$ (**e**), CH_2Ph (**f**), Het (**g**); **9**: X = S;

10: R^2 = H; Het =

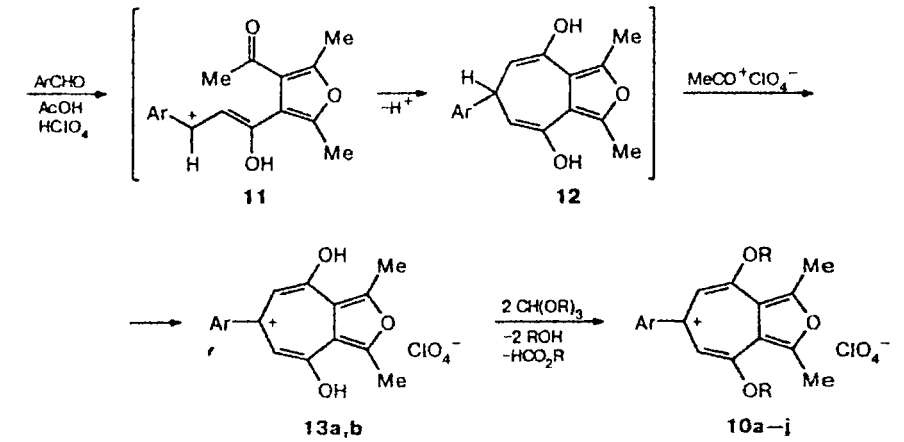


The purposes of this study are, first, optimization of the discovered method for synthesis of cyclohepta[*c*]furylium salts; second, preparation of related N- and S-heteroazulenes, cyclohepta[*c*]pyrrolium and -thiophenium salts; third, search for possibilities of annelation of different cycles to five-membered heterorings.

To achieve the first of these purposes, we considered two directions: (1) formation of 6-arylcyclohepta[*c*]furylium, -pyrrolium, and -thiophenium cations in the absence of trialkyl orthoformate, which allows one to introduce in the reaction any aromatic aldehydes, including those with lowered nucleophilicity of the carbonyl group; and (2) direct arylation of 1,3-dimethyl-4,8-dialkoxycylohepta[*c*]furylium salts **10** (R^1 = Alk, R^2 = H).

Cyclocondensation of bis-ketoenol **6** with aromatic aldehydes in the presence of equimolar amounts of a 16% solution of perchloric acid in acetic acid and acetic anhydride (Scheme 2) gives readily 6-aryl-1,3-dimethyl-4,8-dihydroxycyclohepta[*c*]furylium perchlorates (**13**), which can be isolated and characterized or, if necessary, transformed without isolation into 3,8-dialkoxy-derivatives (**10a—j**) by the addition of the corresponding orthoesters. Since the starting reaction mixture contains no highly-reactive dialkoxymethyl cations formed from an orthoester by the action of perchloric acid, the protonated form of the intermediate 2,5-dimethyl-3,4-di-

Scheme 2



10: R = Me, Ar = 4-$MeOC_6H_4$ (**a**); R = Et, Ar = 4-$MeOC_6H_4$ (**b**); R = Me, Ar = 3+4-$(OCH_2O)C_6H_3$ (**c**); R = Et, Ar = 3+4-$(OCH_2O)C_6H_3$ (**d**); R = Me, Ar = 3,4-$(MeO)_2C_6H_3$ (**e**); R = Et, Ar = 3,4-$(MeO)_2C_6H_3$ (**f**); R = Me, Ar = Ph (**g**); R = Et, Ar = Ph (**h**); R = Et, Ar = 4-ClC_6H_4 (**i**); R = Et, Ar = 4-$NO_2C_6H_4$ (**j**)

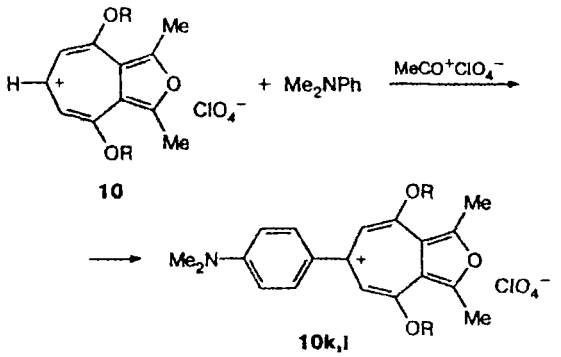
13: Ar = Ph (**a**); 4-ClC_6H_4 (**b**)

acetylfuran 7 [14] reacts directly with aromatic aldehyde to form protonated chalcone (**11**), which is transformed into 6-aryl-1,3-dimethylcyclohepta[*c*]furan-4,8-dione (**12**) *via* intramolecular cyclization. The latter is dehydrated to form perchlorates **13** (see Scheme 2). Under the same conditions, using electron-enriched aromatic aldehydes (anisaldehyde, *etc.*), we obtained perchlorates **10a—j**, some of which were identical to those synthesized previously.[14]

It is known[16,17] that pyrilium and benzopyrilium salts without substituents in position 4 are arylated by electron-enriched compounds to form 4-aryl-substituted derivatives. It follows from the results of quantum-chemical calculations of the model bicyclic framework and 4,8-dialkoxy-6-aryl-1,3-dimethylcyclohepta[*c*]furanium cation by the PM-3 method (Table 1) that the atoms in positions 4, 6, and 8 of the seven-membered ring are maximally electron deficient. Positions 4 and 8 occupied by alkoxyl substituents are prone to nucleophilic attack in hydrolysis and aminolysis reactions.[15] We have established that the nucleophilic attack at position 6 of the cyclohepta[*c*]furanium cation is also possible. For example, when salts **10** (R^1 = Alk, R^2 = H) are heated with *N,N*-dimethylaniline in acetic anhydride (Scheme 3), 4,8-dialkoxy-1,3-dimethyl-6-(4-dimethylaminophenyl)cyclohepta[*c*]furanium perchlorates are formed (**10k,l**).

It follows from Scheme 2 that the formation of the pyrrole and thiophene fragments should be preliminarily (or directly, during the cyclocondensation of bis-ketoenol **6**) provided for the synthesis of N- and S-heteroazulenes. Fusion of bis-ketoenol **6** with primary arylamines, 5-amino-1,3-dimethylpyrrolo[3,2-*d*]pyrimidine-2,4-dione,[18] or aliphatic amine acetates (ammonium acetate) is the optimum method for the synthesis of 2,5-dimethyl-3,4-diacetylpyrroles **8**. The data on the yields and physicochemical and analytical parameters of diacetylpyrroles **8a—g** are presented in Table 2.

Scheme 3

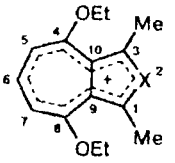


10: R = Me (**k**), Et (**l**)

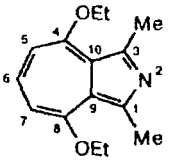
The temperature regime of fusion of arylamines and bis-ketoenol **6** should be strictly controlled, since on heating at temperatures higher than 180 °C, 3,4-diacetylpyrroles **8** are transformed into 2-aryl-1,3,6-trimethylcyclopenta[*c*]pyrrol-4-ones by intramolecular cyclization. The transformation observed (Scheme 4) is an unusual[19] and, most likely, the simplest method for preparing azapentalenone **17**.

Even short heating of solutions of equimolar quantities of diacetylpyrroles **8a—g** and 70% perchloric acid in excess triethyl orthoformate results in the formation (Scheme 5) of previously unknown 1,3-dimethyl-2-R-4,8-diethoxycyclohepta[*c*]pyrrolium perchlorates (**14a—f**). The synthesis can be performed in one pot, fusing first bis-ketoenol **6** with the chosen amine or its acetate and then adding orthoformate and perchloric acid (see Scheme 5, X = N—R). 1,3-Dimethyl-4,8-diethoxycyclo-

Table 1. Results of the PM3 quantum-chemical calculation of charges on atoms of cyclohepta[*c*]furanium **10a**, cyclohepta[*c*]pyrrolium **14a—c,f**, and cyclohepta[*c*]thiophenium cations **15a** and 2-azaazulene **16**



10, 14, 15



16

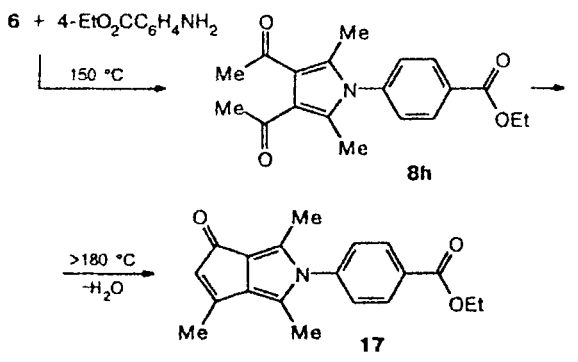
Compound	X	C(1), C(3)	X(2)	C(4), C(8)	C(5), C(7)	C(6)	C(9), C(10)
10	O	1.101	−0.011	0.369	−0.334	0.212	−0.183
14a	N—H	−0.179	0.453	0.345	−0.315	0.182	−0.126
14b	N—Me	−0.166	0.420	0.345	−0.317	0.180	−0.127
14c	N—(4-MeC_6H_4)	−0.167	0.505	0.348	−0.331	0.185	−0.138
14f	N—Het	[a]	0.354	0.357	−0.336	0.195	[a]
15a	S	−0.200	0.506	0.343	−0.340	0.213	−0.121
16	N	−0.085	−0.061	0.178	−0.210	0.003	−0.098

[a] Since two heterocycles in compound **14f** are not strictly orthogonal, the charges on the atoms nearest to the N atom of pyrrole differ substantially: C(1), −0.134; C(3), −0.082; C(9), −0.127; C(10), −0.150.

Table 2. Parameters of 1-R-2,5-dimethyl-3,4-diacetylpyrroles (**8a—g**)

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	N	Empirical formula	IR, ν/cm^{-1}	^{1}H NMR, δ
8a	77.3	180—181	67.13 / 67.02	7.25 / 7.31	7.85 / 7.82	$C_{10}H_{13}NO_2$	3207, 3167, 1687	2.28 (s, 6 H); 2.38 (s, 6 H); 8.84 (s, 1 H)
8b	53.7	140—141	68.51 / 68.37	7.34 / 7.82	7.21 / 7.25	$C_{11}H_{15}NO_2$	1660, 1633	2.31 (s, 6 H); 2.36 (s, 6 H); 3.39 (s, 3 H)
8c	66.0	134—135	75.23 / 75.81	7.12 / 7.12	5.22 / 5.20	$C_{17}H_{19}NO_2$	1673, 1640	2.06 (s, 6 H); 2.39 (s, 6 H); 2.40 (s, 3 H); 7.01 (d, 2 H); 7.28 (d, 2 H)
8d	63.2	119—120	72.21 / 71.56	6.52 / 6.71	4.95 / 4.91	$C_{17}H_{19}NO_3$	1673, 1646	2.06 (s, 6 H); 2.40 (s, 6 H); 3.85 (s, 3 H); 6.98 (d, 2 H); 7.06 (d, 2 H)
8e	63.3	160—161	71.53 / 71.09	6.41 / 6.71	10.35 / 10.42	$C_{16}H_{18}N_2O_2$	3433, 3340, 3233, 1633	2.00 (s, 6 H); 2.33 (s, 6 H); 4.93 (s, 2 H); 6.67 (t, 1 H); 6.90 (q, 2 H); 7.20 (t, 1 H)
8f	41.0	83—84	75.56 / 75.81	7.15 / 7.11	5.24 / 5.20	$C_{17}H_{19}NO_2$	1660, 1640	2.24 (s, 6 H); 2.38 (s, 6 H); 5.03 (s, 2 H); 6.88 (d, 2 H); 7.21—7.32 (m, 3 H)
8g	16.2	265—266	60.25 / 60.66	5.60 / 5.66	15.65 / 15.72	$C_{18}H_{20}N_4O_4$	1710, 1690, 1675, 1660	2.09 (s, 6 H); 2.44 (s, 6 H); 3.36 (s, 3 H); 6.21 (d, 1 H); 7.06 (d, 1 H)

Scheme 4



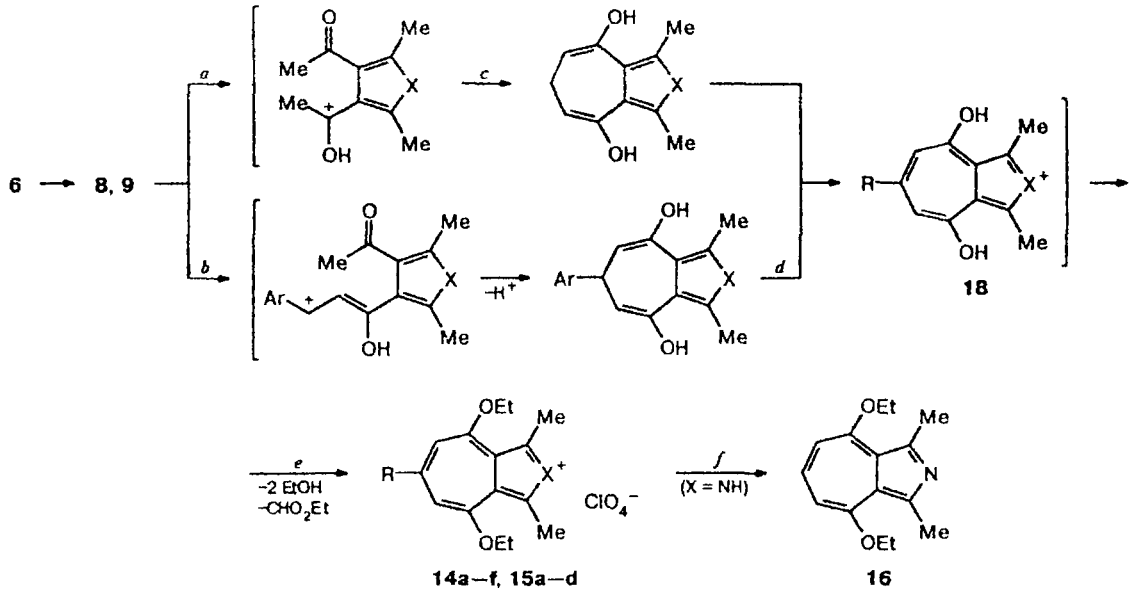
hepta[*c*]thiophenium perchlorate (**15a**) was obtained similarly by heating an acetic-acid solution of bis-ketoenol **6** in a hydrogen sulfide flow followed by the action of triethyl orthoformate and perchloric acid (see Scheme 5, X = S). Anhydrous potassium perchlorate in acetone deprotonates 1,3-dimethyl-2*H*-4,8-diethoxycyclohepta[*c*]pyrrolium perchlorate **14a**, and the azulene heteroanalog, 1,3-dimethyl-4,8-diethoxy-2-azaazulene (**16**), was thus obtained for the first time.

The most optimum variant of preparing 6-aryl-substituted S-heteroazulenes is the condensation of aromatic aldehydes and diacetylthiophene **9** (preliminarily synthesized from bis-ketoenol **6**) under the action of 16% perchloric acid in acetic anhydride followed by treatment with an orthoester. Using 4-dimethylaminocinnamic aldehyde as an example, we demonstrated that unsaturated aldehydes (*cf.*, transformations of cyclohepta[*c*]furanium salts[14]) can be used in the reaction as well. Unlike O-heteroazulenes (cyclohepta[*c*]furanium salts **10**), we failed to isolate 4,8-dihydroxycyclohepta[*c*]thiophenium salts **18** in the crystalline state directly from the reaction medium, most likely due to the formation of mixtures of mono- and bis-*O*-acetates in the medium of acetaldehyde. However, after the treatment of these mixtures with triethyl orthoformate, crystalline products of *O*-ethylation of the hydroxy-derivatives, 4,8-diethoxycyclohepta[*c*]thiophenium perchlorates **15b—d** (X = S), were easily isolated in 20—30% yield.

The IR spectra of perchlorates **14a—f** and **15a—d** contain absorption bands in the regions of 1620—1640, 1570—1590, 1200—1250, and 1050—1150 cm^{-1}, which are typical of C=N, C=C, C—OC, and ClO bonds, respectively.[20] A singlet from two methyl groups in the region of 2.8—2.9 ppm and signals from aromatic protons in the region of 7.2—7.8 ppm were detected in the ^{1}H NMR spectra of compounds **14a—f** and **15a—d**. The signals of protons at the seven-membered cycle appear in the region of 6.5—8.2 ppm, and they exhibit a slight upfield shift (by 0.15—0.25 ppm) as compared to those of cyclohepta[*c*]furanium perchlorates of type **10**, while the signals of methyl groups at the pyrrole and thiophene cycles exhibit a downfield shift (by 0.1—0.15 ppm), which indicates, perhaps, a greater participation of nitrogen and sulfur atoms in delocalization of the positive charge (see Table 1). The displacement of the positive charge to the heteroatom in perchlorates **14** and **15** passivates 4,8-ethoxy groups in reactions with nucleophilic reagents. As in cyclohepta[*c*]furanium cations **10** (R^1 = Alk, R^2 = H), the maximum positive charge in 2-azaazulene **16** is concentrated on atoms in positions 4 and 8 of the seven-membered cycle, which leads to an increase in the capability of this compound to react with nucleophilic substrates.

Under the action of sodium hydrocarbonate in aqueous propan-2-ol, perchlorates **14** and **15** are hydrolyzed

Scheme 5

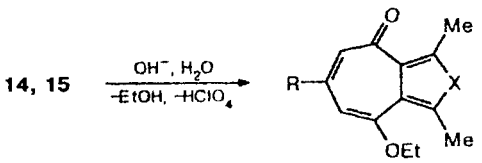


14a—f, 15a—d **16**

14: R = H, X = N—R′, R′ = H (**a**), Me (**b**), 4-MeC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), CH_2Ph (**e**), Het (**f**)
15: X = S; R = H (**a**), Ph (**b**), 4-$MeOC_6H_4$ (**c**), 4-$Me_2NC_6H_4CH{=}CH$ (**d**)
Reagents: *a*. ArCHO, $HClO_4$, AcOH; *b*. $HClO_4$; *c*. $CH(OEt)_3$; *d*. $MeCO^+ClO_4^-$; *e*. 2 $CH(OEt)_3$; *f*. K_2CO_3.

to form 1,3-dimethyl-8-ethoxycyclohepta[*c*]pyrrol-4-ones (**19a—d**) and -thiophen-4-ones (**20a,b**) (Scheme 6). In the absence of bases, 2-*H*- and 2-alkylcyclohepta[*c*]pyrrolium perchlorates are practically not hydrolyzed, whereas 2-hetaryl-derivative **14f** is completely transformed into cyclohepta[*c*]pyrrol-4-one **19d**.

Scheme 6



19a—d; 20a,b

19: R = H, X = N—R′; R′ = H (**a**), Me (**b**), 4-MeC_6H_4 (**c**), Het (**d**)
20: X = S; R = H (**a**), 4-$MeOC_6H_4$ (**b**)

It should be mentioned in conclusion that only one method of formation of a similar diethoxytropilium cycle is known in which a very exotic synthon, 1,2-diacetylcyclobutadienetricarbonyliron, is used.[21] This method includes two stages: the formation of the corresponding ethoxytropone with triethyl orthoformate and subsequent alkylation of the carbonyl group by triethyloxonium fluoborate. Thus, it is evident that a simple and efficient general method for the one-pot or, as a maximum, two-stage synthesis of O-, N-, and S-heteroanalogs of azulene with the axial symmetry of structures has been found. This method allows wide variations of substituents in positions 4, 6, and 8 of the seven-membered cycle in the cyclohepta[*c*]pyrrolium, -furanium, and -thiophenium cations and at the N atom of the cyclohepta[*c*]pyrrolium cation.

Experimental

IR spectra of the compounds obtained were recorded on a Specord IR-71 spectrometer in Nujol. ^1H NMR spectra were recorded on Varian VXR-300 and Bruker DPX-250 spectrometers: for compounds **13b** and **10a,g—j**, in CD_3CN; for compounds **8a—d,f,g**; **10b—f,k**; **13a**; **14a—f**; **15a—d**; **16**; and **17**; in $CDCl_3$; and for compounds **7e**; **19a—d**; and **20a,b**, in DMSO-d_6. Elemental analysis was performed in the laboratory of microanalysis in the Scientific-Research Institute of Physical and Organic Chemistry, Rostov State University. The starting tetraketone **6** was obtained by the standard procedure.[18] A solution of 16% perchloric acid in anhydrous acetic acid was prepared by the dropwise addition of 57% perchloric acid (68.03 mL) to acetic anhydride (243.7 mL) with cooling (0—5 °C) and stirring on a magnetic stirrer.

Quantum-chemical calculations of heteroazulenium cations **10**, **14**, and **15** and azaazulene **16** (see Table 1) were performed using the PM3 method within the framework of the computer HyperChem™ program (Release 4 for Windows) kindly presented by Academician N. S. Zefirov and Prof. Yu. A. Ustynyuk (Moscow State University). Melting points, yields, and data of elemental analysis, and IR and ^1H NMR spectroscopy for the compounds obtained are presented in Tables 2—5.

6-Aryl-1,3-dimethyl-4,8-dioxycyclohepta[*c*]furanium perchlorates (13a,b). A mixture of a solution of 3,4-diacetylhexane-2,5-dione **6** (0.01 mol) in a 16% solution (5 mL) of $HClO_4$ in AcOH, Ac_2O (3 mL, 0.03 mol), and aromatic aldehyde

(0.01 mol) were heated for 10 min on a water bath (95 °C), cooled, and diluted with an equal volume of ether. The product formed was filtered off, washed with ethyl acetate and ether, and recrystallized from nitromethane (see Table 2).

6-Aryl-4,8-dialkoxy-1,3-dimethylcyclohepta[*c*]furanium perchlorates (10a—j). ***A*. From 3,4-diacetylhexane-2,5-dione 6.** A mixture of a solution of tetraketone **6** (0.01 mol) of a 16% solution (5 mL, 0.01 mol) of $HClO_4$ in AcOH, Ac_2O (3 mL, 0.03 mol), and aromatic aldehyde (1.1 g, 0.01 mol) was heated for 10 min on a water bath (95 °C) and cooled. Trialkyl orthoformate (20 mL) was added, and the mixture was refluxed for 5 min. Perchlorates **10a—j** were isolated similarly to compounds **13a,b** and purified by recrystallization from AcOH.

B*. From 6-aryl-1,3-dimethyl-4,8-dioxycyclohepta[*c*]furanium perchlorates (13).** A suspension of perchlorate **13** (0.01 mol) in trialkyl orthoformate (20 mL) was refluxed for 5 min and cooled. Perchlorates **10c—l** were isolated as described above. Perchlorates **10c—l** obtained by methods ***A and ***B*** are identical (see Table 3), and the mixing probe did not give a depression of the melting point.

4,8-Dialkoxy-1,3-dimethyl-6-(*N*,*N*-dimethylaminophenyl)cyclohepta[*c*]furanium perchlorates (10k,l). *N*,*N*-Dimethylaniline (1.2 g, 0.01 mol) was added to a solution of 2,8-dimethyl-3,7-dimethoxy(ethoxy)-5*H*-cyclohepta[*c*]furanium perchlorate **10** [11] (0.01 mol) in Ac_2O (10 mL). The mixture was heated for 30 min on a water bath and diluted with an equal volume of ether. Crystals of perchlorates **10k,l** that formed were filtered off and purified by recrystallization from AcOH (see Table 3).

1-R-3,4-Diacetyl-2,5-dimethylpyrroles (8a—g). A mixture of tetraketone **6** (0.01 mol) and aromatic amine or ammonium acetate (0.01 mol) was fused at 150—155 °C for 1.5—2 h on an oil bath to obtain pyrroles **8a—g**, which were purified by recrystallization from propan-2-ol (for compound **8f**, hexane was used) (see Table 2).

2-(4-Carbethoxyphenyl)-1,3,6-trimethylcyclopenta[*c*]pyrrol-4-one (17). A mixture of tetraketone **6** (1.98 g, 0.01 mol) and ethyl 4-aminobenzoate (1.65 g, 0.01 mol) was fused on a bath with Silicon oil at 250 °C until the formation of water ceased (10—15 min). The melt was cooled, and compound **17** was purified by recrystallization from hexane to obtain colorless needles in 80.6% yield (2.5 g), m.p. 126—127 °C. Found (%): C, 73.62; H, 6.24; N, 4.60. $C_{19}H_{19}NO_3$. Calculated (%): C, 73.76; H, 6.19; N, 4.53. IR, ν/cm^{-1}: 1700, 1686, 1606, 1286, 1220. ^1H NMR ($CDCl_3$), δ: 1.40 (t, 3 H); 1.96 (s, 3 H); 2.28 (s, 3 H); 2.40 (s, 3 H); 4.40 (q, 2 H); 6.32 (s, 1 H); 7.24 (t, 2 H); 8.18 (d, 2 H).

1,3-Dimethyl-2-R-4,8-diethoxycyclohepta[*c*]pyrrolium perchlorates (14a—f). 70% $HClO_4$ (0.01 mol) was added dropwise with stirring to 1-R-3,4-diacetyl-2,5-dimethylpyrrole (**8a—g**)

Table 3. Parameters of 4,8-dialkoxy-6*H*(aryl)-1,3-dimethylcyclohepta[*c*]furanium perchlorates (**10c,e—l, 13a,b**)

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	Cl	N	Empirical formula	IR, ν/cm^{-1}	^1H NMR, δ
10c	73.5	229—231	54.70 54.74	4.39 4.36	8.11 8.08	— —	$C_{20}H_{19}ClO_9$	1100, 1253, 1566	2.86 (s, 6 H); 4.33 (s, 6 H); 6.07 (s, 2 H); 6.73 (s, 2 H); 7.01 (d, 1 H); 7.20 (d, 1 H); 7.46 (q, 1 H)
10e	70.6	247—248	55.42 55.45	5.12 5.10	7.83 7.79	—	$C_{21}H_{23}ClO_9$	1100, 1273, 1620	2.83 (s, 6 H); 3.98 (d, 6 H); 4.29 (s, 6 H); 6.71 (s, 2 H); 7.04 (d, 1 H); 7.28 (t, 1 H); 7.40 (q, 1 H)
10f	75.0	233—234	57.04 57.20	5.60 5.64	7.52 7.34	— —	$C_{23}H_{27}ClO_9$	1100, 1206, 1260, 1513, 1580	1.65 (t, 6 H); 2.86 (s, 6 H); 3.86 (s, 3 H); 4.00 (s, 3 H); 4.59 (q, 4 H); 6.68 (s, 2 H); 7.00 (d, 1 H); 7.25 (t, 1 H); 7.42 (q, 1 H)
10g	86.0	263—264	57.73 57.80	4.88 4.85	9.04 8.98	— —	$C_{19}H_{19}ClO_7$	1100, 1553, 1580	2.85 (s, 6 H); 4.31 (s, 6 H); 6.72 (s, 2 H); 7.61 (m, 3 H); 7.78 (t, 2 H)
10h	85.7	256—257	59.51 59.65	5.58 5.50	8.98 8.40	— —	$C_{21}H_{23}ClO_7$	1100, 1273, 1586	1.58 (t, 6 H); 2.90 (s, 6 H); 4.60 (q, 4 H); 6.80 (s, 2 H); 7.64 (m, 3 H); 7.80 (t, 2 H)
10i	85.3	245—246	55.07 55.15	4.95 4.85	15.57 15.51	— —	$C_{21}H_{22}Cl_2O_7$	1100, 1273, 1620	1.60 (t, 6 H); 2.81 (s, 6 H); 4.52 (q, 4 H); 6.85 (s, 2 H); 7.24 (d, 2 H); 7.71 (d, 2 H)
10j	56.5	262—263	53.94 53.91	4.70 4.74	7.61 7.58	2.93 2.99	$C_{21}H_{22}ClNO_9$	1100, 1273, 1620	1.62 (t, 6 H); 2.80 (s, 6 H); 4.45 (q, 6 H); 6.80 (s, 2 H); 7.01 (d, 2 H); 7.78 (d, 2 H)
10k	61.4	248—249	57.56 57.60	5.50 5.52	8.14 8.10	3.22 3.20	$C_{21}H_{24}ClNO_7$	1100, 1253, 1593	2.80 (s, 6 H); 3.21 (s, 6 H); 4.30 (s, 6 H); 6.81 (s, 2 H); 6.92 (d, 2 H); 7.79 (d, 2 H)
10l	53.6	225—227	59.11 59.29	6.18 6.06	7.75 7.61	2.92 3.01	$C_{23}H_{28}ClNO_7$	1090, 1260, 1580	1.64 (t, 6 H); 2.79 (s, 6 H); 3.15 (s, 6 H); 4.64 (q, 4 H); 6.78 (s, 2 H); 6.85 (d, 2 H); 7.84 (d, 2 H)
13a	79.0	284—285	55.59 55.67	4.19 4.12	9.72 9.67	— —	$C_{17}H_{15}ClO_7$	1100, 1580, 3300	2.87 (s, 6 H); 6.81 (s, 2 H); 7.63 (m, 3 H); 7.84 (t, 2 H)
13b	73.7	262—264	50.78 50.89	3.61 3.52	17.72 17.67	— —	$C_{17}H_{14}Cl_2O_7$	1090, 1580, 3285	2.85 (s, 6 H); 6.81 (s, 2 H); 7.08 (d, 2 H); 7.74 (d, 2 H)

(0.01 mol) in triethyl orthoformate (20 mL). The mixture was refluxed for 3—5 min, cooled, and diluted with an equal volume of ether. Perchlorate **14a—f** that formed was filtered off and recrystallized from AcOH (see Table 4).

1,3-Dimethyl-4,8-diethoxy-2-azaazulene (16). A mixture of compound **14a** (0.7 g, 2.03 mmol) and anhydrous potassium carbonate (2 g) in acetone (100 mL) was stirred for 30 min on a magnetic stirrer. The suspension was heated to boiling, filtered off, and cooled. Dark-blue prismatic crystals of azaazulene **16** that formed were filtered off and purified by recrystallization from acetone (yield 0.27 g (54%), m.p. 212—213 °C). Found (%): C, 73.40; H, 7.53; N, 5.32. $C_{15}H_{19}NO_2$. Calculated (%): C, 73.44; H, 7.81; N, 5.38. IR, ν/cm^{-1}: 3100, 1580, 1233. ^1H NMR ($CDCl_3$), δ: 1.48 (t, 6 H); 2.85 (s, 6 H); 4.19 (q, 4 H); 6.10 (d, 2 H); 7.21 (t, 1 H).

1,3-Dimethyl-4,8-diethoxycyclohepta[*c*]thiophenium perchlorate (15a). A hydrogen sulfide flow was bubbled through a solution of tetraketone **6** (0.01 mol) in acetic acid (20 mL) at 60—80 °C for 30 min, and then triethyl orthoformate (20 mL) and 70% $HClO_4$ (0.01 mol) were added dropwise. The mixture was refluxed for 3—5 min, cooled, and diluted with an equal volume of ether. Perchlorate **15a** that formed was filtered off and purified by recrystallization from AcOH (yield 2.7 g (75.0%), m.p. 171—172 °C). Found (%): C, 49.60; H, 5.31; Cl, 9.81; S, 8.80. $C_{15}H_{19}ClSO_6$. Calculated (%): C, 49.65; H, 5.28; Cl, 9.77; S, 8.84. IR, ν/cm^{-1}: 1110, 1280, 1520, 1586. ^1H NMR ($CDCl_3$), δ: 1.43 (t, 6 H); 2.74 (s, 6 H); 4.42 (q, 4 H); 6.61 (s, 1 H); 6.67 (s, 1 H); 7.99 (t, 1 H).

6-Aryl-1,3-dimethyl-4,8-diethoxycyclohepta[*c*]thiophenium perchlorates (15b—d). A hydrogen sulfide flow was bubbled through a solution of tetraketone **6** (0.01 mol) in 20 mL AcOH at 60—80 °C for 30 min, and then a 16% solution of $HClO_4$ (5 mL, 0.01 mol) in AcOH, Ac_2O (3 mL, 0.03 mol), and aromatic aldehyde (1.1 g, 0.01 mol) were added dropwise. The mixture was heated for 10 min with stirring on a water bath (50—60 °C) and cooled. Trialkyl orthoformate (20 mL) was added, and the mixture was refluxed for 5 min. Compounds **15b—d** were isolated and purified similarly to perchlorates **13a,b** (see Table 4).

2-R-1,3-Dimethyl-4-ethoxycyclohepta[*c*]pyrrol-8-ones (19a—d). ***A.* From 2-R-1,3-dimethyl-4,8-diethoxy[*c*]pyrrolium perchlorates 14a—f,h.** A suspension of perchlorate **14** (0.01 mol)

Table 4. Parameters of 4,8-dialkoxy-6*H*(aryl)-1,3-dimethylcyclohepta[*c*]pyrrolium (**14a—f**) and -thiophenium perchlorates (**15a—d**)

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	Cl	N	Empirical formula	IR, ν/cm^{-1}	^1H NMR, δ
14a	82.9	227—228	52.43 52.10	5.56 5.83	10.03 10.25	4.02 4.05	$C_{15}H_{20}ClNO_6$	3193, 1580, 1100	1.63 (t, 6 H); 2.91 (s, 6 H); 4.44 (q, 4 H); 6.53 (d, 2 H); 7.77 (t, 1 H); 12.57 (s, 1 H)
14b	82.6	240—241	53.22 53.41	6.10 6.16	9.56 9.85	3.85 3.89	$C_{16}H_{22}ClNO_6$	1580, 1220, 1086	1.62 (t, 6 H); 2.92 (s, 6 H); 3.95 (s, 3 H); 4.50 (q, 4 H); 6.80 (d, 2 H); 8.00 (t, 1 H)
14c	53.0	202—203	60.51 60.62	6.40 6.01	8.10 8.13	3.20 3.21	$C_{22}H_{26}ClNO_6$	1280, 1220, 1086	1.60 (t, 6 H); 2.50 (s, 3 H); 2.59 (s, 6 H); 4.51—4.59 (m, 4 H); 6.92 (d, 2 H); 7.10 (d, 2 H); 7.44 (d, 2 H); 8.14 (t, 1 H)
14d	71.0	210—212	58.93 58.47	5.96 5.80	7.75 7.85	3.14 3.10	$C_{22}H_{26}ClNO_7$	1286, 1220, 1093	1.61 (t, 6 H); 2.86 (s, 6 H); 3.81 (s, 3 H); 4.60 (m, 4 H); 6.76 (d, 2 H); 7.05 (d, 2 H); 7.59 (d, 2 H); 8.05 (t, 1 H)
14e	67.8	226—227	60.46 60.62	6.25 6.01	8.32 8.13	3.17 3.21	$C_{22}H_{26}ClNO_6$	1246, 1206, 1086	1.59 (t, 6 H); 2.83 (s, 6 H); 4.48—4.56 (m, 4 H); 5.69 (s, 2 H); 6.85 (d, 2 H); 6.87 (d, 2 H); 7.27—7.37 (m, 3 H); 8.06 (t, 1 H)
14f	70.0	249—252	53.01 52.83	5.58 5.20	6.53 6.78	11.50 11.52	$C_{23}H_{27}ClN_4O_8$	1110, 1243, 1683, 1724	1.59 (t, 6 H); 2.56 (s, 6 H); 3.29 (s, 3 H); 3.56 (s, 3 H); 4.39—4.56 (m, 4 H); 6.35 (d, 1 H); 6.73 (d, 2 H); 7.70 (d, 1 H); 7.96 (t, 1 H)
15a	75.0	171—172	49.60 49.65	5.31 5.28	9.81 9.77	—	$C_{15}H_{19}ClO_6S$	1110, 1280, 1520, 1586	1.43 (t, 6 H); 2.74 (s, 6 H); 4.42 (q, 4 H); 6.61 (s, 1 H); 6.67 (s, 1 H); 7.99 (t, 1 H)
15b	24.0	193—195	57.40 57.46	5.22 5.28	—	—	$C_{21}H_{23}ClO_6S$	1093, 1266, 1540, 1606	1.46 (t, 6 H); 2.75 (s, 6 H); 4.45 (q, 4 H); 6.61 (s, 2 H); 7.40—7.55 (m, 5 H)
15c	31.3	194—196	56.29 56.34	5.32 5.37	—	—	$C_{22}H_{25}ClO_7S$	1100, 1273, 1546, 1593	1.40 (t, 6 H); 2.75 (s, 6 H); 3.39 (s, 3 H); 4.36 (q, 4 H); 6.54 (s, 2 H); 6.86 (d, 2 H); 7.52 (d, 2 H)
15d	25.5	208—209	59.03 59.10	5.89 5.95	—	—	$C_{25}H_{30}ClNO_6S$	1100, 1286, 1573, 1606	1.40 (q, 6 H); 2.62 (s, 6 H); 3.12 (s, 6 H); 4.40 (q, 4 H); 6.18 (s, 2 H); 7.30 (d, 1 H); 7.35 (d, 2 H); 7.66 (d, 1 H); 7.78 (d, 2 H)

Table 5. Parameters of cyclohepta[*c*]pyrrol-8-ones (**19a—d**) and cyclohepta[*c*]thiophen-8-ones (**20a,b**)

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	N	Empirical formula	IR, ν/cm^{-1}	^{1}H NMR, δ
19a	75.0	245—246	71.62 71.87	6.53 6.96	6.42 6.45	$C_{13}H_{15}NO_2$	3180, 3140, 1620, 1593	1.38 (t, 3 H); 2.51 (s, 3 H); 2.56 (s, 3 H); 4.01 (q, 2 H); 5.58 (d, 1 H); 5.94 (d, 1 H); 6.70 (d, 1 H); 11.96 (s, 1 H)
19b	93.3	138—139	72.75 72.70	7.36 7.41	6.03 6.06	$C_{14}H_{17}NO_2$	1620, 1580, 1213	1.40 (t, 3 H); 2.60 (s, 3 H); 2.68 (s, 3 H); 3.56 (s, 3 H); 4.03 (q, 2 H); 5.65 (d, 1 H); 5.99 (d, 1 H); 6.70 (d, 1 H)
19c	76.0	150—151	78.54 78.15	6.67 6.89	4.51 4.56	$C_{20}H_{21}NO_2$	1620, 1580, 1207	1.36 (t, 3 H); 2.29 (s, 3 H); 2.34 (s, 3 H); 2.40 (s, 3 H); 4.04 (q, 2 H); 5.70 (d, 1 H); 6.03 (d, 1 H); 6.75 (d, 1 H); 7.18 (d, 2 H); 7.39 (d, 2 H)
19d	91.0	253—254	63.52 63.95	5.78 5.62	14.23 14.22	$C_{21}H_{22}N_4O_4$	3127, 1700, 1647, 1627	1.39 (t, 3 H); 2.23 (s, 3 H); 2.29 (s, 3 H); 3.13 (s, 3 H); 3.45 (s, 3 H); 4.07 (q, 2 H); 5.78 (d, 1 H); 6.07 (d, 1 H); 6.62 (d, 1 H); 6.80 (d, 1 H); 7.78 (d, 1 H)
20a	72.6	64—65	66.59 66.64	6.05 6.02	12.09 12.13	$C_{13}H_{14}SO_2$	1286, 1560, 1613, 1693	1.25 (t, 3 H); 2.41 (s, 3 H); 2.48 (s, 3 H); 3.72 (q, 2 H); 5.30 (d, 1 H); 5.72 (d, 1 H); 6.48 (q, 1 H)
20b	61.7	101—103	70.45 70.56	5.98 5.92	9.36 9.42	$C_{20}H_{20}SO_3$	1280, 1546, 1620, 1680	1.25 (t, 3 H); 2.39 (s, 3 H); 2.48 (s, 3 H); 3.60 (s, 3 H); 3.85 (q, 2 H); 5.50 (d, 1 H); 6.05 (d, 1 H); 6.67 (d, 2 H); 7.24 (d, 2 H)

and $NaHCO_3$ (1 g) in aqueous propan-2-ol (1 : 1, 40 mL) was refluxed for 15 min, and the alcohol was distilled off. Pyrrolo[*c*]tropones **19a—d** obtained on cooling were filtered off, washed with cold water (10 mL), and purified by recrystallization from acetonitrile.

B. **From 2-azaazulene 16.** Compound **19a** (0.12 g, 67.8%) similar to that obtained from perchlorate **14a** was obtained by refluxing of 2-azaazulene (0.2 g, 0.82 mmol) in water (40 mL) for 30 min. The mixing probe did not give a depression of the melting point (see Table 5).

6-R-1,3-Dimethyl-4-ethoxycyclohepta[*c*]thiophen-8-ones (20a,b). Sodium acetate (0.02 mol) in water (20 mL) was added to a solution of cyclohepta[*c*]thiophenium perchlorate **17** (0.01 mol) in acetone (20 mL). The mixture was heated on a water bath for 1.5—2 h, the acetone was distilled off, and the mixture was cooled. Yellow crystals of tropones **20a,b** were filtered off, washed with water, and purified by recrystallization from aqueous methanol (1 : 1) (see Table 5).

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