Synthesis of carbonyl compounds based on the products of addition of polyhaloalkanes to unsaturated systems. Reactions of 1-aryl-5,5-dichloropenta-2,4-dien-1-ones with ethyl acetoacetate

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The reactions of 1-aryl-5,5-dichloropenta-2,4-dien-1-ones with ethyl acetoacetate in the presence of EtONa give ethyl 4-aryl-6-(2,2-dichlorovinyl)-4-hydroxy-2-oxocyclohexanecarboxylates. The structures of the reaction products were confirmed by ^1H and ^{13}C NMR spectroscopy and by X-ray diffraction analysis.

Key words: ethyl 4-aryl-6-(2,2-dichlorovinyl)-4-hydroxy-2-oxocyclohexanecarboxylates, synthesis; 1-aryl-5,5-dichloropenta-2,4-dien-1-ones; ethyl acetoacetate; condensation; cyclization; crystal structure; ^1H and ^{13}C NMR spectra.

Previously[1] we have shown that the products of condensation of aryl methyl ketones with β,β-dichloroacrolein, *viz.*, 1-aryl-5,5-dichloropenta-2,4-dien-1-ones (**1**), can be regarded as analogs of chalcones. It follows from analysis of the ^{13}C NMR spectra of compounds **1**[1] that nucleophiles would attack most probably the C(3) atom in these compounds (for the ^{13}C NMR spectrum of chalcone, see Ref. 2). Previously we have synthesized 3-aryl-5-(2,2-dichlorovinyl)-1-phenyl-2-pyrazolines by the reaction of compounds **1** with phenylhydrazine (N-nucleophile).[1] In the present work, we studied reactions of pentadienones **1** with ethyl acetoacetate (C-nucleophile).

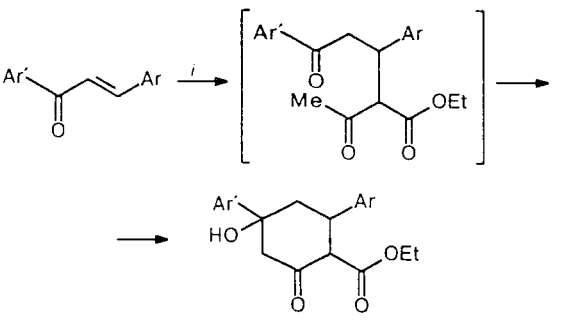
In the known examples in which chalcones reacted with ethyl acetoacetate[3,4] in the presence of bases (EtONa, PrONa, Et_3N), Michael adducts could not be isolated, due to the fast subsequent condensation involving the methyl group of the acetyl fragment and the carbonyl group of chalcone (Scheme 1).

We found that the reactions of 1-aryl-5,5-dichloropenta-2,4-dien-1-ones (**1a—f**) with ethyl acetoacetate in anhydrous EtOH in the presence of EtONa at ~20 °C also afford ethyl 4-aryl-6-(2,2-dichlorovinyl)-4-hydroxy-2-oxocyclohexanecarboxylates **2a—f** (Scheme 2).

The attempts to prepare a similar compound based on 2-(3,3-dichloroallylidene)-1-tetralone were unsuccessful, probably, due to steric hindrance.

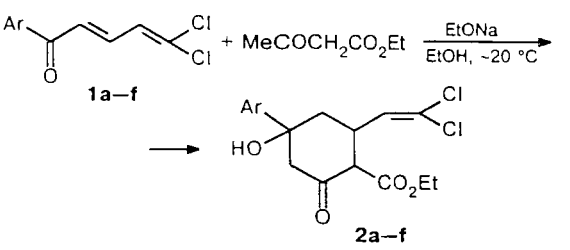
The ^1H and ^{13}C NMR spectra of compounds **2a—f** were studied (Tables 1 and 2). The signals were assigned

Scheme 1



Ar = 2-furyl; 5-methyl-2-furyl; C_6F_5;
Ar' = 2-furyl; 5-methyl-2-furyl; Ph
i = $MeCOCH_2COEt$, base.

Scheme 2



Ar = Ph (**a**); 3-BrC_6H_4 (**b**); 4-ClC_6H_4 (**c**); 4-$EtOC_6H_4$ (**d**); 4-MeC_6H_4 (**e**); 2-thienyl (**f**).

†Deceased.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 522—527, March, 1997.

1066-5285/97/4603-0501 $18.00

Table 1. ^{13}C NMR spectra of compounds **2a—f** (DMSO-d_6), δ

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C=O	OCH_2	CH_3	=CH	$=CCl_2$	Ar
2a*	59.9	196.4	52.8	75.2	40.8	38.0	168.7	60.4	14.1	131.6	120.0	147.4 (*ipso*), 128.2 (C_o), 124.6 (C_m), 127.0 (C_p)
2b	59.8	203.2	52.5	74.9	40.5	37.9	168.7	60.5	14.2	131.4	120.1	150.0 (C-1′), 121.8 (C-3′), 130.5 (C-4′), 129.9 (C-5′), 127.6 (C-2′), 123.7 (C-6′)
2c	59.9	203.2	52.6	75.0	40.6	38.0	168.7	60.5	14.2	131.4	120.1	146.1 (C_{ipso}), 128.1 (C_o), 126.7 (C_m), 136.0 (C_p)
2d	59.8	203.5	53.0	74.9	41.0	38.0	168.7	60.7	14.1	131.6	119.8	139.4 (C_{ipso}), 126.0 (C_o), 113.9 (C_m), 157.4 (C_p), 63.0 (OCH_2), 14.7 (CH_3).
2e	59.9	203.5	52.9	75.1	40.9	38.1	168.8	60.4	14.2	131.6	119.9	144.5 (C_{ipso}), 128.7 (C_o), 124.5 (C_m), 136.0 (C_p), 20.6 (CH_3)
2f	59.7	197.3	53.5	73.3	41.5	37.5	168.4	60.3	14.0	131.2	120.0	152.9 (C-2′), 122.4 (C-5′), 126.8 (4′), 124.4 (C-3′)

* $^{13}C—^{1}H$ spin-spin coupling constants/Hz: $^{1}J_{C(1),H(1)}$ = 129.5 (br.d); $^{1}J_{C(6),H(6)}$ = 144.4; $^{1}J_{C(5),H(5)}$ = 131.3 (br.t); $^{1}J_{C(3),H(3)}$ = 123.8 (td); $^{1}J_{=CH}$ = 163.3 (dm); $^{2}J_{HC=CCl_2}$ = 6.1 (dd); $^{1}J_{OCH_2}$ 147.7 (t); $^{1}J_{CH_3}$ = 124.4 (q).

Table 2. ^{1}H NMR spectra of compounds **2a—f** (DMSO-d_6), δ, spin-spin coupling constants (Hz)*

Compound	$H_a(1)$	$H_e(3)$	$H_a(3)$	$H_e(5)$	$H_a(5)$	$H_a(6)$	H_b	OH	Ar	J/Hz
2a	3.77 d	2.38 dd	3.12 d	1.78 ddd	2.23 dd	3.65 m	6.08 d	5.58 s	7.28 (t, 1 H, H(4′)); 7.38 (t, 2 H, H(3′), H(5′)); 7.48 (t, 2 H, H(2′), H(6′))	$J_{H_a(1)H_a(6)}$ = 11.8; $J_{H_e(3)H_a(3)}$ = 13.8, $J_{H_e(3)H_a(5)}$ = 1.9; $J_{H_e(5)H_a(5)}$ = 13.2; $J_{H_e(5)H_a(6)}$ = 2.9; $J_{H_a(5)H_a(6)}$ = 12.0; $J_{H_a(6)H_b}$ = 9.6
2b	3.75 d	2.38 dd	3.07 d	1.77 dd	2.22 dd	3.62 m	6.08 d	5.80 s	7.35 (m, 1 H, H(5′); 7.45 (m, 2 H, H(4′), H(6′)); 7.67 (s, 1 H, H(2′))	$J_{H_a(1)H_a(6)}$ = 11.8; $J_{H_e(3)H_a(3)}$ = 15.0; $J_{H_e(5)H_a(5)}$ = 13.7; $J_{H_a(6)H_b}$ = 9.3
2c	3.78 d	2.29 dd	3.16 d	1.78 dd	2.20 dd	3.62 m	6.10 d	5.76 s	7.40 (d, 2 H, H(2′), H(6′)); 7.50 (d, 2 H, H(3′), H(5′))	$J_{H_a(1)H_a(6)}$ = 11.6; $J_{H_e(3)H_a(3)}$ = 13.7; $J_{H_e(5)H_a(5)}$ = 12.6; $J_{H_a(6)H_b}$ = 9.3
2d	3.74 d	2.35 dd	3.16 d	1.78 dd	2.19 dd	3.62 m	6.08 d	5.57 s	1.31 (t, 3 H, CH_3); 4.01 (q, 2 H, CH_2) 6.88 (d, 2 H, H(2′), H(6′)); 7.37 (d, 2 H, H(3′), H(5′));	$J_{H_a(1)H_a(6)}$ = 11.8; $J_{H_e(3)H_a(3)}$ = 13.5, $J_{H_e(5)H_a(5)}$ = 12.5; $J_{H_a(6)H_e(5)}$ = 2.1, $J_{H_a(6)H_a(5)}$ = 12.1; $J_{H_a(6)H_b}$ = 9.6
2e	3.75 d	2.37 dd	3.08 d	1.77 dd	2.18 dd	3.60 m	6.08 d	5.62 s	2.27 (s, 3 H, CH_3) 7.14 (d, 2 H, H(2′), H(6′)); 7.35 (d, 2 H, H(3′), H(5′);	$J_{H_a(1)H_a(6)}$ = 11.4; $J_{H_e(3)H_a(3)}$ = 13.7; $J_{H_e(3)He(5)}$ = 2.3; $J_{H_e(5)H_a(5)}$ = 12.5; $J_{H_e(5)H_a(6)}$ = 3.4; $J_{H_a(6)H_b}$ = 9.3
2f	3.75 d	2.28 dd	3.08 d	1.77 dd	2.21 dd	3.64 m	6.10 d	6.37 s	7.22 (dd, 1 H, H(4′)); 7.73 (d, 1 H, H(3′)); 7.83 (d, 1 H, H(5′))	$J_{H_a(1)H_a(6)}$ = 12.0; $J_{H_e(3)H_a(3)}$ = 13.6; $J_{H_e(3)H_e(5)}$ = 3.0; $J_{H_e(5)H_a(5)}$ = 13.2; $J_{H_a(6)H_b}$ = 9.4

* Signals of the COOEt group protons: 4.1 (m, CH_2), 1.2 (t, CH_3, J = 7 Hz).

using selective heteronuclear double resonance and taking into account the multiplicities of the signals and the effects of the corresponding substituents on the chemical shifts of the C and H atoms in the aromatic ring. Cyclic β-oxoesters **2a—f** are capable of being converted into enol forms; therefore, the NMR spectra of these compounds were measured in DMSO-d_6, which stabilizes the keto-forms of β-oxoesters.[5]

The spectra of compounds **2a—f**, in conformity with the structure proposed for them, exhibit doublets at 59.7—59.9 ppm (C(1)) and at 37.5—38.1 ppm (C(6)). The triplets at 40.5—41.5 and 52.5—53.5 ppm were assigned to the C(5) and C(3) atoms, respectively. The signal of the carbonyl group in the cyclohexane ring is manifested in the 195—204 ppm range. The quaternary carbon atom in position 4 is responsible for the singlet at 73.3—75.2 ppm. The dichlorovinyl fragment accounts for the signals at 131.2—131.6 ppm (doublet, =CH) and at 119.8—120.1 ppm (singlet, $=CCl_2$). The signals corresponding to the aromatic fragment were assigned taking into account the effects of substituents on the chemical shifts of unsubstituted benzene.[6]

The ^{1}H NMR spectrum (see Table 2) of compound **2a** contains a signal for $H_a(1)$ as a doublet with the spin-spin coupling constant $^3J_{H_a(1),H_a(6)}$ = 11.8 Hz, corresponding to the *trans*-diaxial arrangement of the $H_a(1)$ and $H_a(6)$ atoms.[4] The signal at 3.65 ppm due to $H_a(6)$ is a multiplet owing to the coupling with $H_a(1)$ and H_b atoms and with the protons at C(5). The high-field signal of the proton at the C(3) atom (2.38 ppm) is additionally split at the $H_e(5)$ proton (1.78 ppm, $^4J_{H_e(5),H_e(3)}$ = 1.9 Hz) due to the so-called "W-effect".[7]

The signals of $H_e(3)$ and $H_e(5)$ are manifested in a higher field than the signals corresponding to axial protons, which is typical of cyclohexanone derivatives.[8] The broadened signal at δ 5.58 in the spectrum of **2a** can be attributed to the OH-group proton (in the ^{1}H NMR spectra of compounds **2a—f** recorded in $CDCl_3$, the signals of the OH-group protons are manifested at 2.0—2.5 ppm).

It is noteworthy that the methylene protons in the ester group are magnetically nonequivalent; this is due to their vicinity to the asymmetrical center at C(1). This CH_2 group is manifested as a multiplet corresponding to an ABX_3 system.

The ^{1}H NMR spectra of compounds **2a—f** recorded in DMSO-d_5 do not change with time. However, the ^{1}H NMR spectra of compound **2a** in $CDCl_3$ or C_6D_6 point to the presence of the enol form; it is responsible for the signal at 13.0 ppm due to the enol OH group (*cf.* Ref. 9). The proportions of the tautomeric forms were determined from the ratio of the intensities of the signals corresponding to the protons of the dichlorovinyl moiety in the ketone (5.45 ppm) and enol (5.32 ppm) forms. In a freshly prepared solution of compound **2a** in C_6D_6, the ketone/enol ratio amounted to 84 : 16 and over a period of three days it changed to 50 : 50.

Despite the fact that compounds **2a—f** contain three asymmetrical carbon atoms, they are formed as single diastereomers with the e,e,e-orientation of the Ar, $-CH=CCl_2$, and CO_2Et groups.

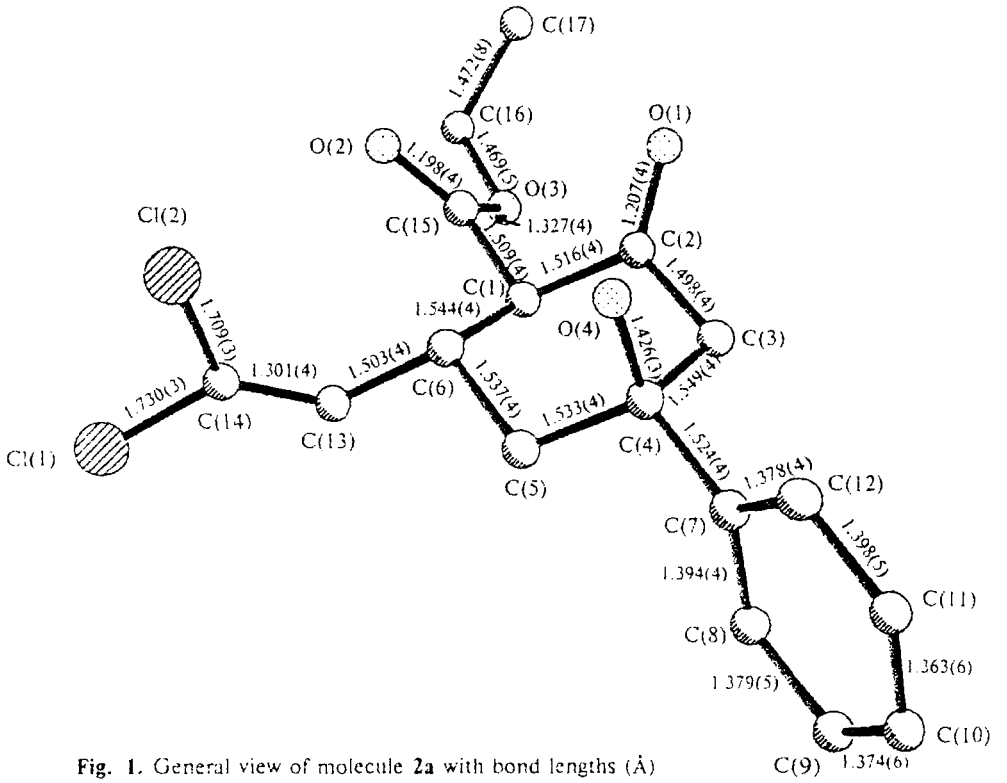


Fig. 1. General view of molecule **2a** with bond lengths (Å)

Table 3. Bond angles in molecule **2a**

Angle	ω/deg	Angle	ω/deg
C(15)—O(3)—C(16)	116.9(3)	C(6)—C(13)—C(14)	126.4(3)
O(1)—C(2)—C(1)	121.7(2)	C(7)—C(8)—C(9)	121.2(3)
O(1)—C(2)—C(3)	123.3(2)	C(7)—C(12)—C(11)	121.0(3)
C(1)—C(2)—C(3)	114.9(2)	C(8)—C(7)—C(12)	117.6(3)
C(1)—C(6)—C(5)	109.9(2)	C(8)—C(9)—C(10)	120.4(4)
C(1)—C(6)—C(13)	110.4(2)	C(9)—C(10)—C(11)	119.6(4)
C(2)—C(1)—C(6)	108.4(2)	C(10)—C(11)—C(12)	120.3(4)
C(2)—C(1)—C(15)	110.4(2)	Cl(1)—C(14)—Cl(2)	112.9(2)
C(2)—C(3)—C(4)	111.1(2)	Cl(1)—C(14)—C(13)	122.8(3)
C(3)—C(4)—C(7)	109.5(2)	Cl(2)—C(14)—C(13)	124.3(3)
C(4)—C(7)—C(8)	120.7(3)	O(2)—C(15)—O(3)	124.8(3)
C(4)—C(7)—C(12)	121.7(3)	O(2)—C(15)—C(1)	124.5(3)
C(5)—C(4)—C(3)	110.0(2)	O(3)—C(15)—C(1)	110.8(3)
C(5)—C(4)—C(7)	111.8(2)	O(3)—C(16)—C(17)	109.5(4)
C(5)—C(6)—C(13)	109.7(2)	O(4)—C(4)—C(5)	104.9(2)
C(6)—C(1)—C(15)	113.1(2)	O(4)—C(4)—C(3)	108.6(2)
C(6)—C(5)—C(4)	113.1(2)	O(4)—C(4)—C(7)	112.0(2)

The molecular and crystal structures of compound **2a** were determined by X-ray diffraction analysis. Figure 1 shows the general view of molecule **2a** with bond lengths; the bond angles are listed in Table 3.

In this molecule, the substituted cyclohexane ring occurs in a chair conformation: the C(2) and C(5) atoms deviate from the plane of the four other atoms (accurate to within ±0.020 Å) by −0.636 and 0.660 Å, respectively. The equatorial phenyl and dichlorovinyl substituents are rotated with respect to the planar fragment through angles of 96.7° and 67.6°, respectively. The magnitudes of the C(16)O(3)C(15)C(1) (−178.2°) and C(15)O(3)C(16)C(17) (87.7°) torsion angles indicate that the equatorial CO_2Et group is "twisted".

In the crystal, molecules **2a** are joined by O(4)—H(4)...O(1) (−*x*, −*y*, 1−) intermolecular hydrogen bonds (O(4)...O(1) 2.806(4), O(4)—H(4) 0.83(2), H(4)...O(1) 2.01(2) Å, the O(4)—H(4)...O(1) angle 162(2)°) into centrosymmetrical dimers (Fig. 2). Therefore, the assumption that compounds similar to those under coonsideration incorporate intramolecular double bonds, made in a previous study[3] based on IR-spectroscopy data (for a suspension in vaseline oil), needs to be verified.

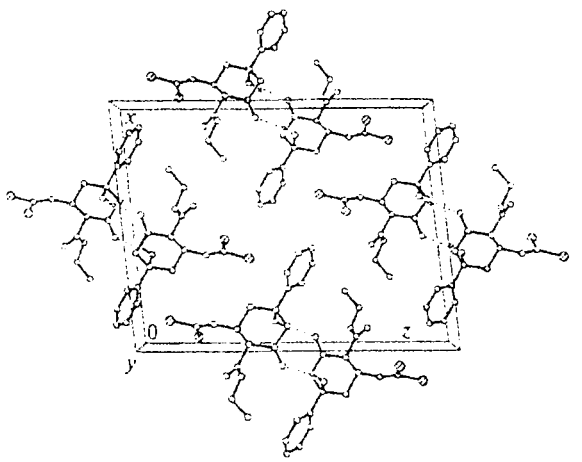
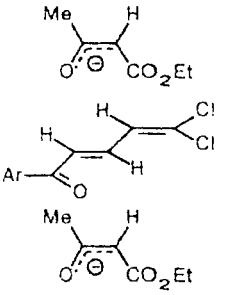


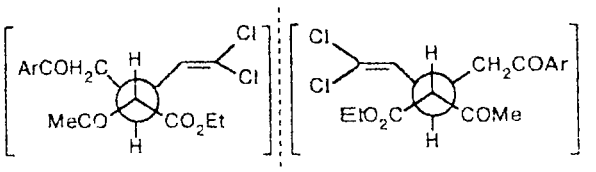
Fig. 2. Crystal structure of compound **2a**

The rest of the geometric parameters of molecule **2a** have their normal magnitudes.[10]

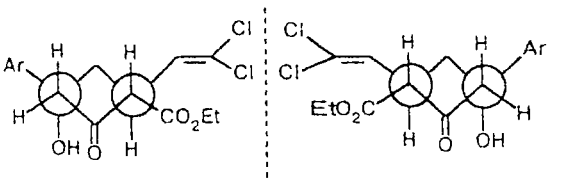
The formation of enantiomers is possible if "planar" compounds **1a—f** are attacked by a nucleophilic species from "above" or from "below":



Apparently, the energetically most acceptable conformation of the Michael adduct is the following:



Further cyclization leads to products **2a—f**, whose geometry is consistent with the results of X-ray diffraction analysis:



Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AC 200P (200 MHz for ^1H and 50.3 MHz for ^{13}C) and Bruker AM-300 (300 MHz for ^1H and 75.47 MHz for ^{13}C) instruments in DMSO-d_6, $CDCl_3$, or C_6D_6. Differentiation of the signals of Me, CH, CH_2, and C_{quater} in the ^{13}C NMR spectra was carried out by the standard JMOD HX.AO procedure.

Melting points were determined on a Boetius hot-stage apparatus and were not corrected. The reactions were monitored by TLC on Silufol UV-254 plates using a hexane—AcOEt mixture (3 : 1 — 1 : 1, v/v) as the eluent.

The unit cell parameters and intensities of 3581 independent reflections were measured on a Siemens P3/PC four-circle automated diffractometer (Mo-Kα, graphite monochro-

Table 4. Coordinates of atoms ($\times 10^4$; for H, $\times 10^3$) in molecule **2a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl(1)	1306(1)	2211(2)	1205(1)	C(9)	3926(3)	1883(7)	5314(2)	H(31)	145(2)	379(7)	479(2)
Cl(2)	562(1)	−1400(2)	1957(1)	C(10)	4079(3)	−44(7)	5714(2)	H(32)	91(2)	209(6)	517(1)
O(1)	−462(1)	2827(4)	4446(1)	C(11)	3460(3)	−1733(7)	5702(2)	H(8)	306(2)	331(7)	463(2)
O(2)	−819(2)	2956(5)	2764(1)	C(12)	2673(2)	−1507(6)	5288(2)	H(9)	436(3)	298(9)	531(2)
O(3)	−686(2)	6417(4)	3267(1)	C(13)	1166(2)	2510(5)	2542(1)	H(10)	466(3)	−23(8)	599(2)
O(4)	1169(1)	−1411(3)	4361(1)	C(14)	1038(2)	1267(6)	1991(1)	H(11)	353(2)	−324(8)	602(2)
C(1)	429(2)	3753(5)	3559(1)	C(15)	−426(2)	4286(6)	3145(2)	H(12)	224(2)	−294(7)	529(2)
C(2)	268(2)	3031(5)	4276(1)	C(16)	−1526(3)	7156(9)	2914(3)	H(13)	150(2)	390(6)	249(2)
C(3)	1078(2)	2538(5)	4740(1)	C(17)	−2241(4)	6516(15)	3323(3)	H(161)	−156(3)	675(9)	249(2)
C(4)	1652(2)	692(5)	4429(1)	H(4)	88(2)	−160(7)	469(2)	H(162)	−176(4)	862(14)	316(3)
C(5)	1809(2)	1368(6)	3699(1)	H(1)	74(2)	499(6)	360(1)	H(171)	−221(3)	708(10)	380(3)
C(6)	956(2)	1828(5)	3243(1)	H(6)	58(2)	44(6)	321(1)	H(172)	−225(7)	474(21)	337(5)
C(7)	2508(2)	410(5)	4882(1)	H(51)	215(2)	23(6)	351(2)	H(172)	−276(3)	699(9)	308(2)
C(8)	3147(2)	2125(6)	4909(2)	H(52)	219(2)	278(6)	371(1)				

mator, $\theta/2\theta$-scanning to $\theta_{max} = 28°$). The crystals of compound **2a** are monoclinic; at 20 °C: $a = 15.354(2)$, $b = 5.793(3)$, $c = 19.705(4)$ Å, $b = 95.96(2)°$, $V = 1745(1)$ Å^3, $d_{calc} = 1.360$ g cm^{-3}, space group $P2_1/n$, $Z = 4$. The structure was solved by the direct method which revealed all the nonhydrogen atoms and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms over 2404 reflections with $I > 3\sigma(I)$. All the H atoms were objectively revealed by differential syntheses and refined isotropically. The final residual values were $R = 0.049$ ($R_w = 0.049$). All calculations were carried out using the SHELXTL PLUS program (the PC version).[11] The coordinates of atoms are listed in Table 4 (the thermal parameters of the atoms are available from the authors).

1-Aryl-5,5-dichloropenta-2,4-dien-1-ones (1a, 1c—f) were prepared by known procedures.[12,13]

1-(3-Bromophenyl)-5,5-dichloropenta-2,4-dien-1-one (1b) was prepared similarly to the procedure described previously[12] by condensation of *m*-bromoacetophenone with 3,3-dichloropropenal, m.p. 69.0—71.5 °C, yield 63%. Found (%): C, 43.22; H, 2.44; Br, 26.39; Cl, 23.42. $C_{11}H_7BrCl_2O$. Calculated (%): C, 43.17; H, 2.31; Br, 26.11; Cl, 23.17. ^{1}H NMR ($CDCl_3$), δ: 6.70 (dd, 1 H, H(2)); 6.98 (dd, 1 H, H(4)); 7.56 (dd, 1 H, H(3) $J_{H(2),H(3)} = 11.1$ Hz, $J_{H(2),H(4)} = 0.6$ Hz, $J_{H(3),H(4)} = 15.2$ Hz); 7.36 (t, 1 H, H(5′)); 7.70 (ddd, 1 H, H(4′)); 7.85 (ddd, 1 H, H(6′)); 8.05 (dd, 1 H, H(2′)); $J_{H(4'),H(5')} = J_{H(5'),H(6')} = 7.8$ Hz, $J_{H(4'),H(6')} = 1.0$ Hz, $J_{H(2'),H(4')} = J_{H(2'),H(6')} = 1.7$ Hz.

Table 5. Characteristics of ethyl 4-aryl-4-hydroxy-6-(2,2-dichlorovinyl)-2-oxocyclohexanecarboxylates **2a—f**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	Cl	Molecular Formula
2a	71	155—156.5	57.42 / 57.15	5.27 / 5.08	20.20 / 19.85	$C_{17}H_{18}Cl_2O_4$
2b*	77	126.0	46.79 / 46.82	4.02 / 3.93	16.00 / 16.26	$C_{17}H_{17}BrCl_2O_4$
2c	88	122.0	51.97 / 52.13	4.41 / 4.37	26.57 / 27.15	$C_{17}H_{17}Cl_3O_4$
2d	95	103—104	56.42 / 56.87	5.96 / 5.53	17.76 / 17.67	$C_{19}H_{22}Cl_2O_5$
2e	85	118.0	57.75 / 58.23	5.39 / 5.43	19.48 / 19.10	$C_{18}H_{20}Cl_2O_4$
2f**	89	98—99	49.50 / 49.46	4.35 / 4.70	19.86 / 19.47	$C_{15}H_{16}Cl_2O_4S$

* For compound **2b**: Br (%): found 18.03; calculated 18.34.
** For compound **2f**: S (%): found 8.98; calculated 8.80.

Ethyl 4-aryl-6-(2,2-dichlorovinyl)-4-hydroxy-2-oxocyclohexanecarboxylates 2a—f (general procedure). Ethyl acetoacetate (30 mmol) was added with stirring to a solution of EtONa (prepared by dissolution of 80 mg of Na in 40—50 mL of anhydrous EtOH). Then a solution of 1-aryl-5,5-dichloropenta-2,4-dien-1-one (**1a—f**) (10 mmol) in 15—20 mL of anhydrous EtOH was added with stirring; the mixture was stirred for 2—3 h, kept for 10 h, and evaporated *in vacuo*. The residue was dissolved in 10—15 mL of EtOH and carefully poured into 50—60 mL of water. The precipitate was filtered off, dried, and crystallized from aqueous EtOH. Characteristics of the products are listed in Table 5.

The work was partly supported by the Russian Foundation for Basic Research (Projects No 95-03-09748 and No 94-03-08338).

References

1. A. A. Dudinov, S. A. Voznesenskii, I. S. Poddubnyi, B. I. Ugrak, L. I. Belen'kii, and M. M. Krayushkin, *Khim. Geterotsikl. Soed.*, 1995, 1511 [*Chem. Heterocycl. Compd.*, 1995 (Engl. Transl.)].
2. V. V. Negrebetskii and A. V. Reznichenko, *Zh. Obshch. Khim.*, 1993, **63**, 1374 [*J. Gen. Chem.*, 1993, **63** (Engl. Transl.)].
3. E. B. Usova, L. I. Lysenko, G. D. Krapivin, and V. G. Kul'nevich, *Khim. Geterotsikl. Soed.*, 1996, 639 [*Chem. Heterocycl. Compd.*, 1996 (Engl. Transl.)].
4. N. I. Orlova, T. N. Gerasimova, M. A. Kudinova, and A. I. Tolmachev, *Zh. Org. Khim.*, 1992, **27**, 1289 [*J. Org. Chem.*, 1992, **27** (Engl. Transl.)].
5. Ch. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Verlag-Chemie, Weinheim, 1988.

6. G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley, New York, 1972.
7. H. Günter, *NMP Spectroscopy. An Introduction*, J. Wiley and Sons, Chichester, 1980, 2nd Edition, VCH, 1988.
8. B. I. Ionin, B. A. Ershov, and A. I. Kol'tsov in *YaMR-spektroskopiya v organicheskoi khimii* [*NMR Spectroscopy in Organic Chemistry*], Khimiya, Leningrad, 1983, 153 (in Russian).
9. N. N. Shapet'ko, Yu. S. Bogachev, S. S. Berestova, V. G. Medvedeva, A. P. Skoldinov, and N. N. Shigorin, *Teor. i Eksp. Khim.* [*Theor. Exp. Chem.*], 1981, **17**, 186 (in Russian).
10. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
11. W. Robinson and G. M. Sheldrick, in: *Crystallographic Computing — Techniques and New Technologies*, Oxford Univ. Press, Oxford, 1988, 366.
12. L. I. Zakharkin and L. P. Sorokina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1958, 1445 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1958, **7** (Engl. Transl.)].
13. L. P. Sorokina, and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 73 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1964, **13** (Engl. Transl.)].

Received August 14, 1996;
in revised form December 27, 1996