Furylcyclohexenones
3.* Synthesis and properties of 6-acetyl-3(5)-furylcyclohex-2-enones. Molecular and crystal structure of 6-acetyl-3-(2-furyl)-5-phenylcyclohex-2-enone

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6-Acetyl-3(5)-furylcyclohex-2-enones were prepared by condensation of furan-containing chalcones with acetylacetone. Acetylcyclohex-2-enones were subjected to *C*-methylation. Studies by IR and ^{1}H NMR spectroscopy demonstrated that the resulting compounds occur predominantly in the enol form both in solutions and in the crystalline state. The molecular structure of 6-acetyl-3-(2-furyl)-5-phenylcyclohex-2-enone was established by X-ray diffraction analysis.

Key words: 6-acetylcyclohex-2-enone, tautomerism, enol form, ketone form, *C*-methylation, IR spectra, ^{1}H NMR spectra, X-ray diffraction analysis, molecular structure.

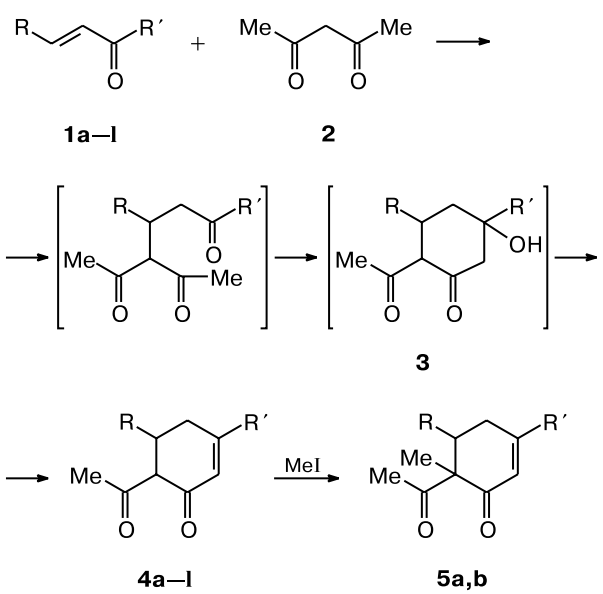
Cyclohexenones attract attention as synthons for the preparation of new derivatives of antibiotics and heterocycles.[2—5] Earlier,[6,7] cyclohexenones have been synthesized from furan-containing chalcones and acetoacetic ester. In the present study, we synthesized acetylcyclohexenones from chalcones **1** and acetylacetone (**2**).

The conventional conditions for the Michael addition at the activated double bond of CH acids, under which CH acids act as both the reagent and solvent,[8] proved to be unsuitable for the reactions of compounds **1** with **2** because attempts to isolate their reaction products failed. Hence, condensation of chalcones **1** with compound **2** was carried out in *n*-butanol in the presence of triethylamine at 100 °C for 1.5—2 h. The reactions of ketones **1** with compound **2** (Scheme 1) directly afforded cyclohexenones **4** as products of dehydration of ketols **3**. In this case, attempts to terminate the reaction in the step of formation of cyclic adducts **3** by decreasing the reaction time and/or decreasing the reaction temperature were unsuccessful.

Cyclohexenones **4** were prepared as yellowish crystalline compounds soluble in most of organic solvents (Table 1).

The ^{1}H NMR spectra of compounds **4** have a signal for the protons of only one COMe group, which confirms their cyclic structures, and signals assigned to the protons of the alicycle and substituents R and R′ (Table 2).

Scheme 1



1, **4:** R = 2-furyl (**a**, **e**, **h**, **k**), Ph (**b**, **f**, **j**), 4-MeO-C_6H_4 (**c, g**), 4-Br-C_6H_4 (**d**), 5-methyl-2-furyl (**i**, **l**); R′ = 2-furyl (**a—d**), 5-methyl-2-furyl (**e—g**), 2-thienyl (**h—j**), Ph (**k**, **l**)
5: R = 2-furyl (**a**, **b**); R′ = 2-furyl (**a**), 2-thienyl (**b**)

* For Part 2, see Ref. 1.

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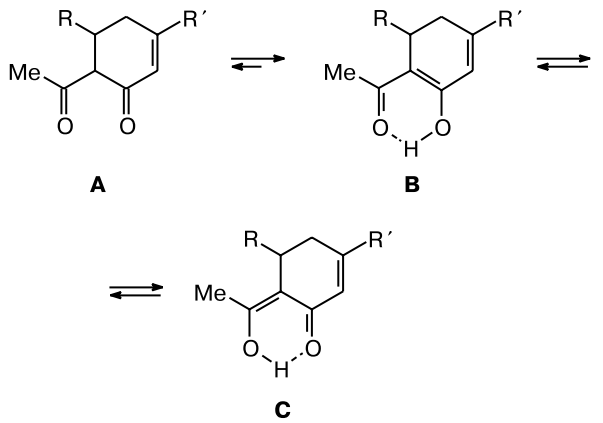
Table 1. Physicochemical and spectroscopic characteristics of 6-acetylcyclohex-2-enones **4a—l** and **5a,b**

Compound	M.p. /°C	Yield (%)	Found / Calculated (%)			Molecular formula	UV, λ_{max}/nm (log ε)	IR, ν/cm^{-1}
			C	H	Br (S)			
4a	121—123	57.5	71.12 71.10	5.25 5.22	—	$C_{16}H_{14}O_4$	223 (4.30), 327 (4.36), 370 (4.64)	3130, 1600
4b	129—132	66.7	77.09 77.12	5.71 5.75	—	$C_{18}H_{16}O_3$	214 (4.07), 312 (4.02), 325 (4.05), 385 (4.32)	3120, 1610
4c	103—105	49.9	73.55 73.53	5.83 5.85	—	$C_{19}H_{18}O_4$	223 (4.22), 312 (4.04), 324 (4.07), 384 (4.32)	1610
4d	130—132	40.3	60.17 60.19	4.19 4.21	22.26 22.24	$C_{18}H_{15}BrO_3$	311 (3.92), 322 (4.20), 323 (3.47), 382 (4.28)	3100, 1610
4e	114—115	38.1	71.79 71.82	5.69 5.67	—	$C_{17}H_{16}O_4$	214 (4.26), 250 (3.66), 333 (4.05), 385 (4.40)	3110, 1610
4f	135—137	54.8	77.51 77.53	6.19 6.16	—	$C_{19}H_{18}O_3$	214 (4.02), 315 (3.88), 333 (3.99), 392 (4.35)	3080, 1610
4g	126—128	59.3	74.03 74.06	6.23 6.21	—	$C_{20}H_{20}O_4$	208 (4.30), 276 (3.91), 326 (4.07), 382 (4.39)	1600
4h	112—114	39.3	67.14 67.11	4.92 4.93	11.23 11.20	$C_{16}H_{14}O_3S$	222 (4.07), 281 (3.82), 377 (4.28)	3110, 1600
4i	108—110	43.7	67.96 67.98	5.40 5.37	10.65 10.67	$C_{17}H_{16}O_3S$	224 (4.19), 284 (3.85), 375 (4.31)	3110, 1600
4j	140—141	66.7	72.91 72.94	5.46 5.44	10.79 10.82	$C_{18}H_{16}O_2S$	208 (4.30), 276 (3.91), 326 (4.07), 382 (4.39)	1605
4k	77—78	57.6	77.15 77.12	5.72 5.75	—	$C_{18}H_{16}O_3$	218 (4.30), 284 (4.13), 368 (4.28)	3110, 1615
4l	83—84	40.8	77.51 77.53	6.18 6.16	—	$C_{19}H_{18}O_3$	208 (4.27), 221 (4.32), 286 (4.13), 360 (4.29)	3080, 1615
5a	87—88	93.5	71.78 71.82	5.65 5.67	—	$C_{17}H_{16}O_4$	325 (4.43)	3125, 1700, 1650, 1600
5b	68—69	86.6	67.95 67.98	5.36 5.37	10.69 10.67	$C_{17}H_{16}O_3S$	330 (4.43)	3110, 1700, 1650, 1600

One would expect the compounds synthesized to be in keto-enol tautomeric equilibrium (Scheme 2), whose position depends on the concentration of solutions and the nature of the solvent.

Scheme 2



On the one hand, the signal for the H(6) proton of the alicycle is not observed in the ^{1}H NMR spectra of acetylcyclohexenones **4** in acetone-d_6 and, consequently, the percentage of the keto form in the tautomeric mixture is <1%. On the other hand, these spectra have only one resonance for the proton of the OH group, whereas additional signals characteristic of regioisomeric enols are absent. The results of the present study and data reported earlier[9,10] suggest that there is a fast (on the ^{1}H NMR time scale) tautomeric equilibrium between structures **B** and **C** of compounds **4**.

By contrast, the ^{1}H NMR spectra of cyclohexenones **4c,f** in $CDCl_3$ have two sets of signals characterizing the enol and ketone forms (signals for the protons of the acetyl groups of the enol and ketone forms of compounds **4c,f** are observed at δ 1.93, 2.07 and 1.80, 1.93, respectively). A comparison of the integral intensities of the signals for the protons of the methyl groups (we failed to make a correlation between the intensities of the signals for the H(5) and H(6) protons of the alicycle due to overlap of their chemical shifts) demonstrated that the

Table 2. ^{1}H NMR spectra of compounds **4a—l** and **5a,b**

Compound	δ (*J*/Hz)				
	MeCO, 6-Me* (s, 3 H)	H of alicycle	R	R′	OH (s)
4a	2.05	3.07 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 4.17 (dd, 1 H, H(5), $J_{H(4)_\alpha,H(5)}$ = 2.0, $J_{H(4)_\beta,H(5)}$ = 6.5); 6.27 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	5.83 (m, 1 H, H(3)); 6.47 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6, $J_{H(4),H(5)}$ = 2.0); 7.23 (dd, 1 H, H(5), $J_{H(3),H(5)}$ = 1.0, $J_{H(4),H(5)}$ = 2.0)	6.08 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6, $J_{H(4),H(5)}$ = 2.0); 6.80 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 7.50 (d, 1 H, H(5), $J_{H(4),H(5)}$ = 2.0)	16.50
4b	1.95	3.03 (dd, 1 H, $H(4)_\alpha$, $J_{H(4)_\alpha,H(4)_\beta}$ = 16.0, $J_{H(4)_\alpha,H(5)}$ = 2.0); 3.20 (ddd, 1 H, $H(4)_\beta$, $J_{H(2),H(4)_\beta}$ = 2.5, $J_{H(4)_\beta,H(5)}$ = 8.0, $J_{H(4)_\alpha,H(4)_\beta}$ = 16.0); 4.28 (dd, 1 H, H(5), $J_{H(4)_\alpha,H(5)}$ = 2.0, $J_{H(4)_\beta,H(5)}$ = 8.0); 6.47 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.5)	7.20 (m, 5 H, Ph)	6.52 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6, $J_{H(5),H(4)}$ = 1.8); 6.83 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 7.66 (d, 1 H, H(5), $J_{H(5),H(4)}$ = 1.8)	16.70
4c	1.93	2.73—3.14 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 4.00 (m, 1 H, H(5)); 6.50 (m, 1 H, H(2))	3.70 (s, 3 H, MeO); 6.73 (d, 2 H, H(2), H(6), $J_{H(2),H(3)}$ = $J_{H(5),H(6)}$ = 9.0); 7.03 (d, 2 H, H(3), H(5), $J_{H(2),H(3)}$ = $J_{H(5),H(6)}$ = 9.0)	6.63 (d, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6); 6.50 (m, 1 H, H(3)); 7.38 (d, 1 H, H(5), $J_{H(5),H(4)}$ = 2.0)	16.50
4d	1.90	2.70—3.10 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 3.90 (dd, 1 H, H(5), $J_{H(4)_\alpha,H(5)}$ = 2.5, $J_{H(4)_\beta,H(5)}$ = 7.5); 6.40 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.5)	6.90 (d, 2 H, H(2), H(6), $J_{H(2),H(3)}$ = $J_{H(5),H(6)}$ = 9.0); 7.20 (d, 2 H, H(3), H(5), $J_{H(2),H(3)}$ = $J_{H(5),H(6)}$ = 9.0)	6.30 (m, 1 H, H(4)); 6.40 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 7.30 (m, 1 H, H(5))	16.20
4e	2.07	2.73—3.01 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 3.98 (dd, 1 H, H(5), $J_{H(4)_\alpha,H(5)}$ = 2.5, $J_{H(4)_\beta,H(5)}$ = 7.5); 6.28 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	5.78 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 6.03 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6, $J_{H(4),H(5)}$ = 1.8); 7.13 (d, 1 H, H(5), $J_{H(4),H(5)}$ = 1.8)	2.28 (s, 3 H, Me); 5.95 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 6.45 (d, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6)	16.40
4f	1.80	3.00 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 4.70 (m, 1 H, H(5)); 6.53 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	7.05 (m, 5 H, Ph)	2.13 (s, 3 H, Me); 6.00 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 6.53 (d, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6)	16.70
4g	1.93	2.60—3.10 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 3.80—4.10 (m, 1 H, H(5)); 6.40 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	3.63 (s, 3 H, MeO); 6.65 (d, 2 H, H(2), H(6), $J_{H(2),H(3)}$ = $J_{H(5),H(6)}$ = 9.0); 7.03 (d, 2 H, H(3), H(5), $J_{H(2),H(3)}$ = $J_{H(5),H(6)}$ = 9.0)	2.23 (s, 3 H, Me); 5.90 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 6.33 (d, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6)	16.65
4h	2.10	3.12 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 4.10 (m, 1 H, H(5)); 6.32 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	5.87 (dd, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6, $J_{H(3),H(5)}$ = 1.5); 6.10 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6, $J_{H(4),H(5)}$ = 2.0); 7.20 (m, 1 H, H(5))	6.95 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 4.0, $J_{H(4),H(5)}$ = 5.0); 7.20 (m, 1 H, H(3)); 7.30 (dd, 1 H, H(5), $J_{H(3),H(5)}$ = 1.2, $J_{H(4),H(5)}$ = 5.0)	16.50
4i	2.13	2.92 (ddd, 1 H, $H(4)_\alpha$, $J_{H(4)_\alpha,H(4)_\beta}$ = 17.0, $J_{H(4)_\alpha,H(5)}$ = 7.0, $J_{H(4)_\alpha,H(2)}$ = 2.5); 3.33 (dd, 1 H, $H(4)_\beta$, $J_{H(4)_\alpha,H(4)_\beta}$ = 17.0, $J_{H(4)_\beta,H(5)}$ = 2.7); 4.10 (dd, 1 H, H(5), $J_{H(4)_\alpha,H(5)}$ = 7.0, $J_{H(4)_\beta,H(5)}$ = 2.7); 6.40 (d, 1 H, H(2), $J_{H(2),H(4)_\alpha}$ = 2.5)	2.20 (s, 3 H, Me); 5.70 (br.s, 2 H, H(3), H(4))	7.05 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 4.5, $J_{H(4),H(5)}$ = 5.0); 7.28 (dd, 1 H, H(3), $J_{H(3),H(4)}$ = 4.5, $J_{H(3),H(5)}$ = 1.2); 7.38 (dd, 1 H, H(5), $J_{H(3),H(5)}$ = 1.2, $J_{H(4),H(5)}$ = 5.0)	16.42

(*to be continued*)

Table 2 (*continued*)

Compound	δ (*J*/Hz)				
	MeCO, 6-Me* (s, 3 H)	H of alicycle	R	R´	OH (s)
4j	2.00	3.00 (dd, 1 H, $H(4)_\alpha$, $J_{H(4)_\alpha,H(4)_\beta}$ = 17.0, $J_{H(4)_\alpha,H(5)}$ = 3.5); 3.30 (ddd, 1 H, $H(4)_\beta$, $J_{H(4)_\alpha,H(4)_\beta}$ = 17.0, $J_{H(4)_\beta,H(5)}$ = 7.0, $J_{H(2),H(4)_\beta}$ = 2.0); 4.10 (dd, 1 H, H(5), $J_{H(4)_\alpha,H(5)}$ = 3.5, $J_{H(4)_\beta,H(5)}$ = 7.0); 6.50 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	7.25 (m, 5 H, Ph)	7.00 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 4.5, $J_{H(4),H(5)}$ = 5.0); 7.25 (m, 2 H, H(3), H(5))	16.50
4k	2.20	3.20 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 4.10 (dd, 1 H, H(5), $J_{H(4)_\alpha,H(5)}$ = 2.0, $J_{H(4)_\beta,H(5)}$ = 7.0); 6.50 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	5.70 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 6.20 (dd, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6, $J_{H(5),H(4)}$ = 2.0); 7.50 (d, 1 H, H(5), $J_{H(5),H(4)}$ = 2.0)	7.30 (m, 5 H, Ph)	16.30
4l	2.10	2.70—3.20 (m, 2 H, $H(4)_\alpha$, $H(4)_\beta$); 4.60 (dd, 1 H, H(5), $J_{H(4)_\alpha,H(5)}$ = 2.5, $J_{H(4)_\beta,H(5)}$ = 7.5); 6.20 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.5)	2.20 (s, 3 H, Me); 5.60 (m, 2 H, H(3), H(4))	7.20 (m, 5 H, Ph)	16.10
5a	1.47*, 1.88	2.80—3.40 (m, 3 H, $H(4)_\alpha$, $H(4)_\beta$, H(5)); 6.55 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	6.25 (m, 1 H, H(4)); 6.45 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 7.33 (d, 1 H, H(5), $J_{H(5),H(4)}$ = 2.0)	6.25 (m, 1 H, H(4)); 6.70 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 7.53 (d, 1 H, H(5), $J_{H(5),H(4)}$ = 2.0)	—
5b	1.50*, 1.90	3.05 (dd, 1 H, $H(4)_\alpha$, $J_{H(4)_\alpha,H(4)_\beta}$ = 16.0, $J_{H(4)_\alpha,H(5)}$ = 7.0); 3.30—3.60 (m, 1 H, $H(4)_\beta$); 3.60 (m, 1 H, H(5)); 6.50 (d, 1 H, H(2), $J_{H(2),H(4)_\beta}$ = 2.0)	6.20 (d, 1 H, H(4), $J_{H(3),H(4)}$ = 3.6); 6.30 (d, 1 H, H(3), $J_{H(3),H(4)}$ = 3.6); 7.30 (m, 1 H, H(5))	7.10 (m, 1 H); 7.40 (m, 2 H)	—

* For compounds **5a,b**.

percentage of the enol form in the reaction mixture was ~70—75%.

The IR spectra of suspensions of compounds **4** in Nujol mulls indicate that these compounds adopt the enol form in the crystalline state. Thus, absorption bands of the ketone group are observed at low frequencies (1600—1615 cm^{-1}) due to intramolecular hydrogen bonding in the enol structure.[11]

Compounds **4a,h** were alkylated with excess MeI in a mixture of acetone and a 50% KOH solution to prepare *C*-alkylation products **5a,b** (see Scheme 1). The IR spectra of methyl-substituted compounds **5** have two absorption bands of the ketone groups, *viz.*, a high-frequency band assigned to the exocyclic ketone group and a low-frequency band assigned to the endocyclic ketone group conjugated with the double bond (see Table 1). In the ^1H NMR spectra, the resonance for the protons of the introduced Me group is observed at high field (δ 1.5), which confirms the structures of compounds **5**.

For compounds **4a,h**, the percentage of the enol form in various solvents was determined from the results of electronic spectroscopy by subtracting the spectra.[12] Methyl-substituted compounds **5a,b** were used as models of the ketone forms.[13] The percentage of the enol form of cyclohexenones **4a,h** in water, ethanol, and heptane was 52, 60, 64 and 51, 65, 73%, respectively. The percentage of the enol form of compounds **4a,h** is close to the corresponding data for acetylacetone and 2-acetylcyclohexanone.[14—16]

To prove the presence of the enol structure of compounds **4** in the crystalline state and refine the conformation of the alicycle, we carried out single-crystal X-ray diffraction study of 6-acetyl-3-(2-furyl)-5-phenylcyclohex-2-enone (**4b**). The projection of the three-dimensional model of the molecule and the atomic numbering scheme are presented in Fig. 1. Selected interatomic distances and bond angles are given in Tables 3 and 4, respectively.

The alicyclic fragment of molecule **4b** adopts a distorted half-chair conformation characterized by the following puckering parameters: s = 1.766, θ = –42.85°, ψ = 55.5°.[17] The planar fragment of the alicycle (plane *1*) is formed by the C(1), C(2), C(5), and C(6) atoms. The C(3) and C(4) atoms deviate from plane *1* in opposite directions by –0.2210 and 0.3079 Å, respectively.

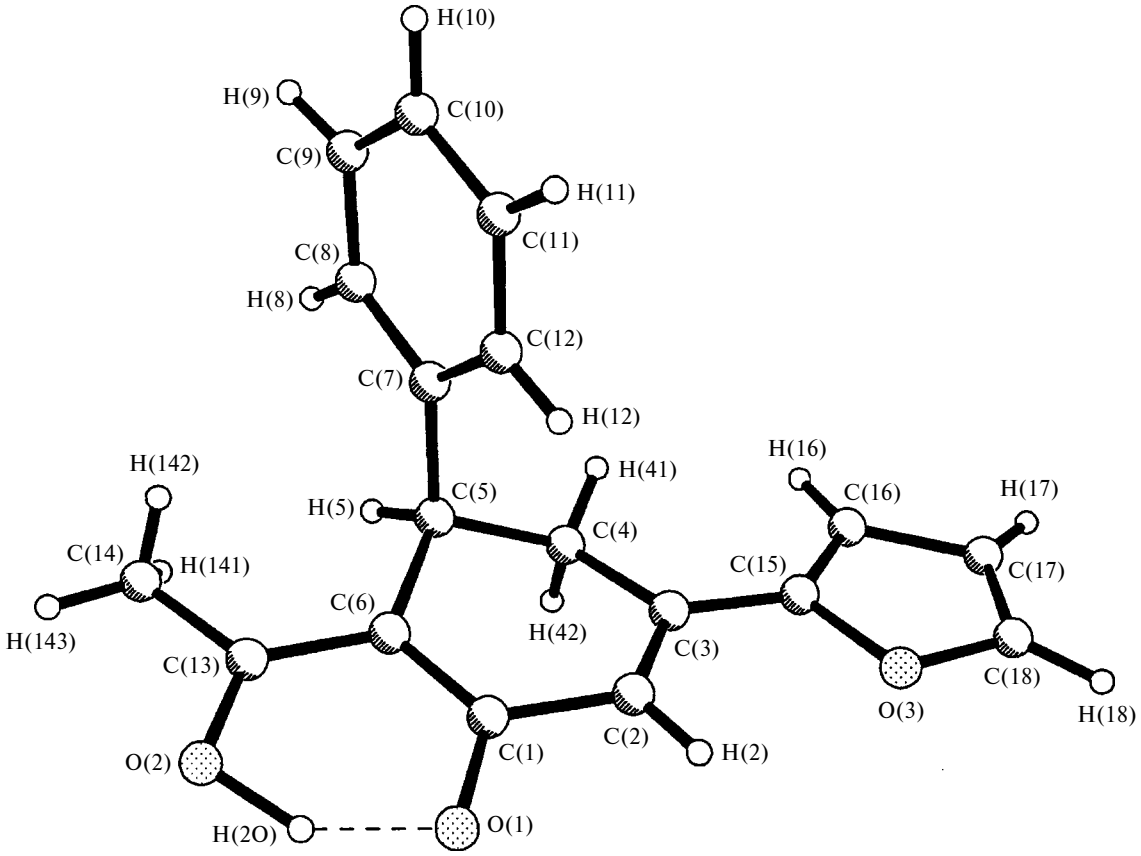


Fig. 1. Projection of the three-dimensional structure of molecule **4b**.

The furan ring is arranged so that the formally double C(15)—C(16) bond eclipses the single C(3)—C(4) bond of the alicycle (the C(4)—C(3)—C(15)—C(16) torsion angle is only 4.5°). Presumably, there is a nonbonded interaction between the O(3) and H(2) atoms because the O(3)—H(2) distance is 2.51 Å, which is smaller than the sum of the van der Waals radii of the O and H atoms (1.40 and 1.16 Å, respectively[18]). The phenyl substituent is in the pseudoaxial position and its C(7)—C(8) bond eclipses the C(5)—H(5) bond (the C(8)—C(7)—C(5)—H(5) torsion angle is 6.8°).

In the crystalline state, molecules **4b** exist in the enol form. The keto-enol fragment of molecule **4b** has a quasicyclic structure due to disorder of the H(20) atom between the O(1) and O(2) atoms. In this structure, the O(1)—C(1), O(2)—C(13) and C(1)—C(6), C(6)—C(13) bond lengths are equalized (1.311(4), 1.289(4) and 1.381(4), 1.405(5) Å, respectively). In the quasicyclic fragment, the O(1), C(1), C(6), C(13), and O(2) atoms are in a single plane (plane *2*) from which the H(20) atom deviates by 0.1921 Å. The angle between planes *1* and *2* is 2.6°.

The crystal packing of molecules **4b** in the unit cell is shown in Fig. 2. It is noteworthy that the furylcyclohexenone fragments of the adjacent molecules are in the antiparallel arrangement. The distance between the antiparallel fragments is 3.4 Å, which is typical of stacking interactions between unsaturated systems.

Table 3. Selected bond lengths (*d*) in molecule **4b**

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(1)	1.311(4)	O(2)—C(13)	1.289(4)
O(1)—C(2)	1.451(5)	C(1)—C(6)	1.381(4)
C(2)—C(3)	1.344(4)	C(3)—C(4)	1.496(4)
C(3)—C(15)	1.436(5)	C(4)—C(5)	1.533(4)
C(5)—C(6)	1.513(4)	C(5)—C(7)	1.527(3)
C(6)—C(13)	1.405(5)		

Table 4. Selected bond angles (ω) in molecule **4b**

Angle	ω/deg	Angle	ω/deg
O(1)—C(1)—C(6)	122.6(3)	C(2)—C(1)—C(6)	121.0(3)
C(1)—C(2)—C(3)	121.9(3)	C(2)—C(3)—C(4)	119.4(3)
C(2)—C(3)—C(15)	123.2(3)	C(4)—C(5)—C(6)	111.9(2)
C(3)—C(4)—C(5)	114.8(2)	C(1)—C(6)—C(13)	119.1(3)
C(4)—C(5)—C(7)	112.3(2)	O(2)—C(13)—C(6)	121.3(3)
C(1)—C(6)—C(5)	119.2(3)	C(6)—C(13)—C(14)	123.3(3)
C(5)—C(6)—C(13)	121.6(3)	O(3)—C(15)—C(3)	117.4(3)
O(2)—C(13)—C(14)	115.4(3)	C(3)—C(15)—C(16)	133.2(3)
O(1)—C(1)—C(2)	116.4(3)		

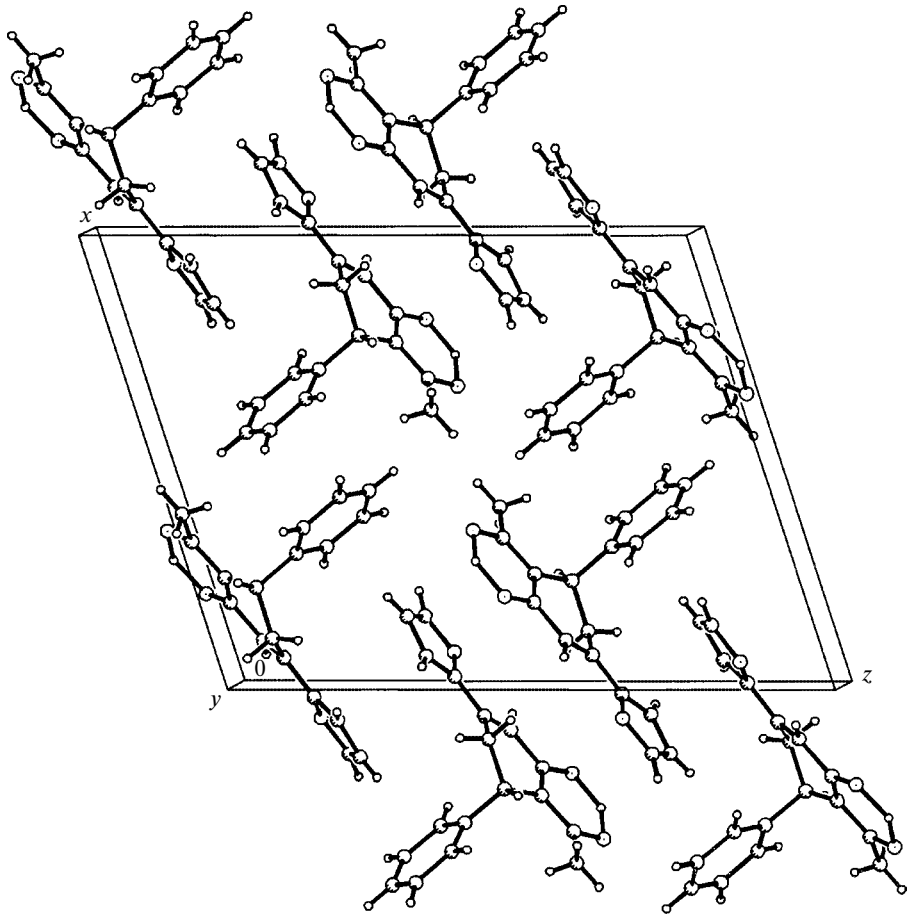


Fig. 2. Crystal packing of molecules **4b** in the unit cell.

Experimental

The electronic spectra were recorded on a UV—Vis instrument for solutions in EtOH. The IR spectra were measured on an IR-71 instrument in Nujol mulls. The ^{1}H NMR spectra were recorded on Tesla BS-467 (60 MHz) and Bruker AC-200P (200 MHz) spectrometers in acetone-d_6 with HMDS and Me_4Si as the internal standards. To determine the percentage of the enol form, the electronic spectra of compounds **4a,h** and **5a,b** were measured in water, ethanol, and heptane on an M-40 instrument.

6-Acetyl-3-(2-furyl)-5-phenylcyclohex-2-enone (4b). A mixture of chalcone **1b** (3 g, 15 mmol), acetylacetone (**2**) (3.0 mL, 30 mmol), and Et_3N (15 mL) in Bu^nOH (30 mL) was kept at 100 °C for 1.5 h. After cooling, the reaction mixture was poured into a beaker containing water (200 mL). After one day, the crystals that formed at the interface were filtered off and washed first with cold EtOH and then with hexane. Cyclohexenone **4b** was obtained in a yield of 3 g (66.7%, from EtOH).

Compounds **4a,c—l** were prepared analogously. Their physicochemical and spectroscopic properties are given in Tables 1 and 2.

6-Acetyl-3,5-di(2-furyl)-6-methylcyclohex-2-enone (5a). Iodomethane (0.4 mL, 6.5 mmol) was added with stirring and cooling to a temperature from 0 to −5 °C to a mixture of a 50% KOH solution (15 mL), acetone (15 mL), and cyclohexenone **4a** (0.95 g, 3.5 mmol). The reaction mixture spontaneously warmed up to 20—25 °C, after which the acetone layer was separated and the aqueous layer was extracted with acetone (15 mL). The acetone was partially evaporated and the mixture was diluted with water. The crystals that formed were filtered off and recrystallized from EtOH. Compound **5a** was isolated in a yield of 0.93 g (93.5%).

Compound **5b** was prepared analogously.

X-ray diffraction study of compound 4b. Crystals suitable for X-ray diffraction study were prepared by repeated crystallization of compound **4b** from EtOH. Pale-yellow crystals with composition $C_{18}H_{16}O_3$ are monoclinic; the unit cell parameters: a = 13.811(3) Å, b = 6.239(1) Å, c = 17.654(4) Å; α = 90.0(3)°, β = 108.16(3)°, γ = 90.00(3)°; V = 1445.4(11) Å^3, d_{calc} = 1.279 g cm^{-3}. The space group is $P2(1)/c$, Z = 4. The X-ray data were collected on an automated Syntex P1 diffractometer (graphite monochromator, Mo-Kα radiation, $\theta/2\theta$ scan technique to $2\theta_{max}$ = 50°) at 293(2) K. A total of 1193 reflections with $I > 3\sigma$ were measured. The structure was solved by direct methods using the SHELXTL program package[19] and refined anisotropically (H atoms were refined isotropically) to R_1 = 0.034 and wR_2 = 0.1011. The complete tables of the bond lengths, bond angles, atomic coordinates, and thermal parameters were deposited with the Cambridge Structural Database.

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