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FURYLCYCLOHEXENONES.

1. SYNTHESIS AND PROPERTIES OF 3- AND 5-FURYL-6-ETHOXYCARBONYLCYCLOHEXENONES

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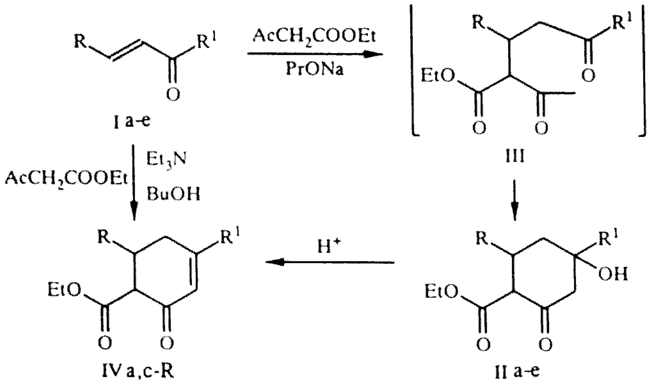
3- and 5-Furylcyclohexenones were obtained by the Michael reaction of furan chalcones with acetoacetic ester. Intermediate β-cycloketols were isolated in many cases. It was found that transformations of β-cycloketols by $HClO_4$ and $TrClO_4$ were a function of the nature of the substituent in position 5 of the alicycle. 5-Arylketols undergo dehydration, while 5-furyl derivatives split both water and the furan fragment, resulting in aromatization of the alicycle. The structure of the synthesized compounds was confirmed by the IR and PMR spectra.

Cyclic chalcones are carriers of different types of biological activity [1, 2]. Synthesists have turned their attention to cyclohexenones as synthons for obtaining *p*-methoxysalicylates — the main structural units of a new class of active antibiotics, Milbemycin-β_3 [3, 4]. However, cyclohexenones containing a furyl residue in the third or fifth position of the alicycle have not been investigated.

We obtained furan cyclohexenones with the Michael reaction of a series of furan ketones (I) with acetoacetic ester (AAE). We investigated the different conditions of addition of AAE to chalcones in the presence of bases: 1) solid KOH in DMSO; 2) KOH in ethanol; 3) sodium alcoholate in AAE; 4) triethylamine (TEA) in butanol.

A difficult to separate mixture of substances was obtained in the first and second variants, and use of the third and fourth variants resulted in different products (Scheme 1). The reaction of chalcones Ia-e with AAE in the presence of sodium alcoholate yielded cycloketols (II) — products of cyclization of 1,5-dicarbonyl adducts (III). However, the conditions of addition of AAE, where the CH acid plays the role of both reagent and solvent (variant 3), could not be used for compounds If-k due to the poor solubility in AAE, so that the conditions of the fourth variant were used for these compounds.

Scheme 1



I-IV a, k R = 2-furyl; b R = 5-methyl-2-furyl; c, e R = C_6H_5; d R = 4-$CH_3O-C_6H_4$; f, i R = 3,4-$(CH_3O)_2-C_6H_3$; g, j R = 4Br$-C_6H_4$; h R = 4-NO_2-C_6H_4; a, b R^1 = C_6H_5; c, d, f-h R^1 = 2-furyl; e, i, j R^1 = 5-methyl-2-furyl; k R^1 = 2-thienyl

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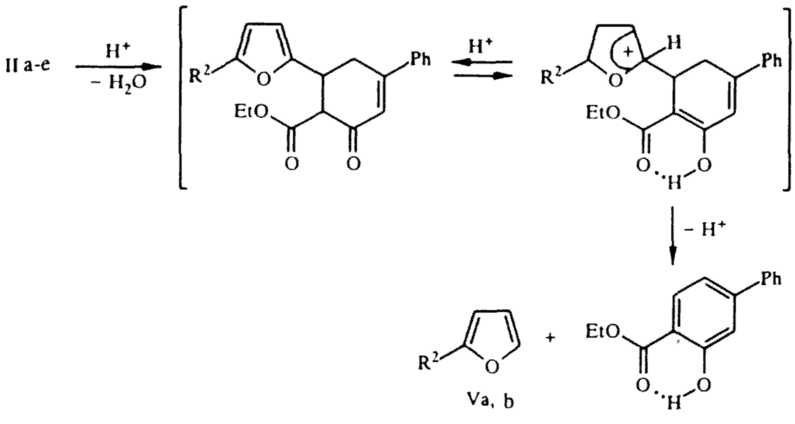
Cyclohexenones (IV) — products of dehydration of ketols II* — are immediately formed in condensation of chalcones Ia-k with AAE in butanol in the presence of TEA. In this case, it was not possible to stop the reaction in the stage of formation of cyclic adducts II by decreasing the duration and/or temperature of the reaction. Compound IVb could not be obtained in *n*-butanol in the presence of TEA.

We also isolated ketones IVc-e as a result of acid-catalyzed dehydration of corresponding ketols IIc-e. Dehydration of ketols IIa, b, which have a furan fragment in position 5 of the alicycle, takes place unusually [5]. Cyclohexenones IVa, b formed split furan (or α-methylfuran) (Va, b) and are converted into ethyl salicylate (VI, Scheme 2).

Scheme 2



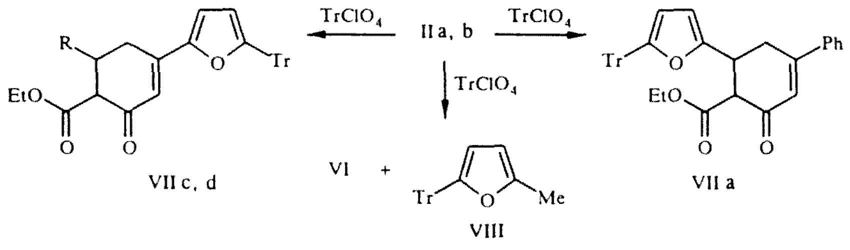
Va R^2 = H, b R^2 = Me

Aromatization of compounds IVa, b probably takes place as a result of electrophilic *unco* attack by a proton in position 2 of the furan ring which is protonated due to its greater π-basicity in comparison to the benzene ring, and by "stealing" a pair of electrons, it acts as a "good" nucleofuge.

We attempted to conduct dehydration and dehydrogenation of compounds IIa-e with preservation of the substituents in positions 3 and 5 of the alicycle using trityl perchlorate ($TrClO_4$) [6, 7]. The experiments conducted showed that the reaction of ketols IIa-e with $TrClO_4$ takes place without separation of hydride ion from the alicycle (Scheme 3). In the case of adducts IIa, c, d containing a 5-unsubstituted furan ring, the trityl group substitutes the hydrogen in position 5 of the furan ring. The perchloric acid liberated during the reaction catalyzes dehydration, resulting in chalcones (VII). Compounds VII were not dehydrogenated by $TrClO_4$.

(5-Methyl-2-furyl)triphenylmethane (VIII) and ethyl salicylate VI are formed in the reaction of ketol IIb, which has a 5-substituted furan fragment in position 5 of the alicycle, with $TrClO_4$, which acts as a 5-methylfuran ring "acceptor." $TrClO_4$ used in both an equimolar amount and in a two-fold excess reacts with ketol IIe as a dehydrating reagent.

Scheme 3



VIIc R = Ph, d R = 4-MeO–C_6H_4

Compounds II, IV, V, VII, VIII are colorless crystalline substances soluble in most organic solvents. The IR spectra of β-ketols II, recorded in petrolatum, have intense absorption bands of ketone (1695-1700 cm^{-1}) and ester (1720-1740 cm^{-1}) carbonyl groups, and there is the absorption band of a hydroxyl group (3350-3420 cm^{-1}) in the high-frequency region (Table

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*The atoms in alicycles II and IV have the same numbering for more convenient comparison of the properties of the compounds.

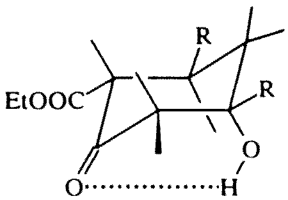

Fig. 1. Predominant conformation of ketols II.

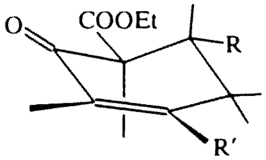

Fig. 2. Predominant conformation of compounds IV, VII.

1). The shape and frequency of absorption of the OH group do not change in the spectra of solutions of compounds II in $CHCl_3$ when they are diluted. The shape and position of the absorption band of the OH group indicates the presence of an intramolecular hydrogen bond in ketols II, in which ketone or ester carbonyls can participate [8]. The calculations performed by the method of molecular mechanics (MMX 89) show the higher probability of a hydrogen bond with a ketone group (the OH...O (ketone) and OH...O (ester) distances are 3.07 and 4.17 Å, respectively).

The PMR spectra of compounds II confirm their cyclic structure (there is no signal from protons of the CH_3CO group) and can be used to judge the conformation of the alicycle (Table 2). Based on the stereospecificity of the spin–spin coupling constants [9-11], it was found that the alicycle in compounds II primarily has a chair conformation. The chair conformation is confirmed by the vicinal SSCC J_{56}, equal to 12.0 Hz. The value of J_{56} = 12.0 Hz indicates the *trans*-biaxial orientation ofthe hydrogen atoms at the 5-C and 6-C atoms and consequently the equatorial position of the ester group and substituent R.

With respect to the environment of the 3-C atom, the OH group, as less bulky than substituent R, probably occupies the axial position in which formation of an intramolecular hydrogen bond is possible, as established by IR spectroscopy (Fig. 1).

The IR spectra of compounds IV, VII have no absorption bands of OH groups and contain bands of moderate intensity caused by stretching vibrations of C=C bonds (1630-1640 cm^{-1}) and intense absorption bands of an ester group (1715 cm^{-1}) and a ketone group conjugated with a double bond (1660 cm^{-1}) (Table 1).

The structure of chalcones IV, VII correspond to the PMR spectra (Table 2). The nonequivalence of the protons at the 4-C atom and the values of the geminal and vicinal SSCC $^3J_{45}$ and $^3J_{4\alpha 4\beta}$ (Table 2) indicate the absence of inversion of the alicycle and its existence primarily in the half-chair conformation (Fig. 2). The signals of the 5-H and 6-H protons are not always permitted, but the $^3J_{56}$ SSCC was determined with the spectra of compounds IVa, h, j. The value of $^3J_{56}$, equal to 12-13 Hz, suggests the identity of the configuration of the environment of 5-C and 6-C atoms in the alicycle in chalcones IV, VII, and ketols II.

Either β-ketols II or cyclohexenones IV are thus the products of addition of acetoacetic ester to chalcones I in different conditions. The last transformation of β-ketols by electrophilic reagents (H^+, $TrClO_4$) takes place differently as a function of the nature of the substituent in position 5 of the alicycle. 5-Arylketols undergo dehydration, while 5-furyl derivatives split both water and the furan fragment, which results in aromatization of the alicycle.

EXPERIMENTAL

The IR spectra were recorded in petrolatum on an IR-71 instrument. The PMR spectra were obtained on Tesla BS-467 (60 MHz) and Bruker AC-200 P spectrometers, HMDS, TMS internal standard. The ^{13}C NMR spectra were recorded on a Bruker AC-200 P, TMS internal standard.

3-Hydroxy-5-phenyl-3-(2-furyl)-6-ethoxycarbonylcyclohexanone (IIc). Here 5 ml of a solution of sodium propylate (0.25 g of sodium in 5 ml of propanol) was added to 15 g (0.12 mole) of AAE, then 9.5 g (0.05 mole) of chalcone Ic was added by small portions while stirring. The mixture was left overnight. The thickened reaction mass was diluted with hexane, neutralized with acetic acid, the sediment was filtered off, and 6.8 g of compound IIc was obtained.

Compounds IIa, b, d e were prepared similarly. The characteristics of ketols IIa-e are given in Tables 1 and 2.

5-Phenyl-3-(2-furyl)-6-ethoxycarbonyl-2-cyclohexenone (IVc). Method 1. Here 1-2 drops of 70% perchloric acid was added to a solution of 2 g (6 mmole) of ketol IIc in 20 ml of benzene. The solution was boiled for 3 h, cooled, and washed with 5% soda solution. The benzene layer was dried over anhydrous sodium sulfate and evaporated at room temperature. The sediment was recrystallized from ethanol, and 1.1 g of compound IVc was obtained. ^{13}C NMR ($CDCl_3$) of compound IVc: 13.60 ($\underline{C}H_3CH_2O$); 32.98 (4-C); 43.55 (5-C); 59.75 ($CH_3\underline{C}H_2O$); 60.73 (6-C); 112.50, 113.41, 119.44, 127.21, 127.40

TABLE 1. Physicochemical Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp, °C	Found, % Calculated, %			IR spectrum, ν, cm^{-1}	Yield, %
			C	H	Br (N, S)		
IIa	$C_{19}H_{20}O_5$	144...145	69,26 69,50	6,42 6,14		3350, 1735, 1700	82
IIb	$C_{20}H_{22}O_5$	112...113	70,49 70,16	6,21 6,48		3410, 1720, 1695	82
IIc	$C_{19}H_{20}O_5$	103...105	69,22 69,50	6,45 6,14		3360, 1730, 1700	43
IId	$C_{20}H_{22}O_6$	123...125	67,37 67,03	6,44 6,19		3390, 1740, 1700	50
IIe	$C_{20}H_{22}O_5$	158...160	70,42 70,16	6,19 6,48		3380, 1740, 1700	45
IVa	$C_{19}H_{18}O_4$	73...74	73,27 73,53	6,06 5,85		3100, 1740, 1670, 1610	80
IVc	$C_{19}H_{18}O_4$	108...109	73,29 73,53	6,09 5,85		1640, 1660, 1715, 3130	59
IVd	$C_{20}H_{20}O_5$	105...107	70,28 70,57	6,15 5,92		1605, 1650, 1720	68
IVe	$C_{20}H_{20}O_4$	98...100	74,33 74,06	5,95 6,21		1640, 1660, 1715	50
IVf	$C_{21}H_{22}O_6$	121...123	68,38 68,10	5,71 5,99		3130, 1750, 1650, 1610	77
IVg	$C_{19}H_{17}BrO_4$	122...124	58,91 58,63	4,09 4,40	20,26 20,53	1740, 1640, 1600	51
IVh	$C_{19}H_{17}NO_6$	119...121	64,51 64,22	4,53 4,82	3,60 3,94	3140, 1720, 1640, 1595	54
IVi	$C_{22}H_{24}O_6$	149...151	68,42 68,74	6,58 6,29		3100, 1730, 1630, 1595	65
IVj	$C_{20}H_{19}BrO_4$	171...173	59,29 59,57	4,53 4,75	20,05 19,81	1750, 1660, 1610	36
IVk	$C_{17}H_{16}O_4S$	102...104	64,29 64,54	5,41 5,10	9,92 10,13	3140, 1730, 1670, 1605	59
VI	$C_{15}H_{14}O_3$	55...56	74,63 74,36	5,48 5,82		1660	82
VIIa	$C_{38}H_{32}O_4$	153...155	82,30 82,58	6,11 5,84		1720, 1640, 1600	91
VIIc	$C_{38}H_{32}O_4$	218...220	82,32 82,58	5,55 5,84		1720, 1640, 1600	85
VIId	$C_{39}H_{34}O_5$	214...216	66,35 66,64	10,29 10,01		1720, 1650, 1600	62
VIII	$C_{24}H_{20}O$	156...158	88,57 88,85	6,48 6,21		3160, 3120, 1590	49

(C_6H_5); 128.12, 128.68, 145.53, and 151.26 (3-C, 4-C, 2-C, 5-C of furan ring); 140.77 (2-C); 145.87 (3-C); 169.08 (1-C); 193.46 ppm ($\underline{C}OOC_2H_5$).

Compounds IVd, e were prepared similarly.

Method 2. A mixture of 3 g (15 mmole) of chalcone Ic, 4 ml (31 mmole) of AAE, and 15 ml (0.107 mole) of TEA in 30 ml of *n*-butanol was held at 100°C for 2 h. It was cooled, poured in water, and left until sediment precipitated. The sediment was filtered off and washed with hexane, and 3 g of compound IVc was obtained.

Compounds IVa, d-k were prepared similarly.

The characteristics of cyclohexanones IVa, c-k are reported in Tables 1 and 2.

2-Hydroxy-4-phenylbenzoic Acid Ethyl Ester (VI). Here 0.5 ml of 70% perchloric acid was added to a solution of 7 g (0.02 mole) of ketol IIa in 50 ml of benzene. The solution was boiled for 10 h, cooled, and washed with an aqueous solution of sodium carbonate and water. The benzene layer was dried over Na_2SO_4 and evaporated at room temperature. The residue was crystallized from ethanol, producing 2 g of compound VI. PMR spectrum (CCl_4): 1.27 (3H, t, $\underline{CH_3}CH_2$, J = 7.0 Hz); 3.93 (2H, q, $CH_3\underline{CH_2}$, J = 7.0 Hz); 6.85 (1H, d.d, 5-H); 7.03 (1H, d, 3-H); 7.62 (1H, d, 6-H, J_{45} = 8.0 Hz, J_{35} = 2.0 Hz); 7.07-7.48 (5H, m, C_6H_5); 10.7 ppm (1H, s, OH). See Table 1 for the other characteristics of acid VI.

TABLE 2. PMR Spectra of the Synthesized Compounds

Compound	δ, ppm, J, Hz				
	OC_2H_5*	alicycle protons	R	R¹	OH
1	2	3	4	5	6
IIa	0,21 t, 4,18 m	2,42 (1H, d.d.d $J_{4\alpha4\beta}$ = 14,0, $J_{4\alpha5}$ = 5,0, $J_{4\alpha2\alpha}$ = 2,5, 4-Hα); 2,50 (1H, d.d, $J_{4\alpha4\beta}$ = 14,0, $J_{4\beta5}$ = 2,5, 4-Hβ); 2,78 (1H, d.d, $J_{2\alpha2\beta}$ = 14,0, $J_{2\alpha4\alpha}$ = 2,5, 2-Hα); 3,03 (1H, d, $J_{2\alpha2\beta}$ = 14,0, 2-Hβ); 3,78 (1H, d, J_{65} = 12,0, 6-H); 4,18 (m, 5-H)	6,13 (1H, d, 3-H), 6,29 (1H, d.d, 4-H), 7,48 (1H, d, 5-H), J_{34} = 3,6, J_{54} = 2,0	7,25...7,55 (5H, m)	2,55 br.s
IIb	0,95 t, 3,90 d	2,38 (1H, d.d.d, $J_{4\alpha4\beta}$ = 14,0, $J_{4\alpha5}$ = 4,5, $J_{4\alpha2\alpha}$ = 2,5, 4-Hα); 2,45 (1H, d.d, $J_{4\alpha4\beta}$ = 14,0, $J_{4\beta5}$ = 2,5, 4-Hβ); 2,73 (1H, d.d, $J_{2\alpha2\beta}$ = 14, $J_{2\alpha4\alpha}$ = 2,5, 2-Hα); 3,00 (1H, d, $J_{2\alpha2\beta}$ = 14,0, 2-Hβ); 3,68 (1H, d, 6-H, J_{56} = 12,0); 4,15 (1H, m, 5-H)	5,82 (1H, m, 4-H); 5,97 (1H, d, 3-H, J_{34} = 3,6); 2,12 (3H, s, CH_3)	7,25...7,60 (5H, m)	2,60 br.s
IIc	0,95 t, 3,85 q	2,20...2,50 (2H, m, 4-Hα, 4-Hβ); 2,63 (1H, d.d, $J_{2\alpha2\beta}$ = 14,0, $J_{2\alpha4\alpha}$ = 2,0, 2-Hα); 3,00 (1H, d.d, $J_{2\alpha2\beta}$ = 14,0, 2-Hβ); 3,72 (1H, d, J_{56} = 13,0, 6-H); 3,91 (1H, m, 5-H)	7,21...7,3 (5H, m)	2,15 (3H, s, CH_3), 6,21 (2H, m, 3-H, 4-H); 7,05 (1H, m, 5-H)	2,93 br.s
IId	0,97 r, 3,88 q	2,2...3,58 (4H, m, 2-Hα, 2-Hβ, 4-Hα, 4-Hβ); 3,58...3,70 (2H, m, 5-H, 6-H)	6,83 (2H, 2-H, 6-H); 7,18 (2H, 3-H, 5-H); J_{23} = J_{56} = 9,0; 3,66 (3H, s, CH_3O)	6,23 (1H, d, 3-H); 6,48 (1H, d.d, 4-H); 7,53 (1H, d, 5-H); J_{34} = 3,6, J_{54} = 2,0	2,83 br.s
IIe	0,95 t, 4,12 m	2,25...2,45 (2H, m, 4-Hα, 4-Hβ); 2,70 (1H, d.d, $J_{2\alpha2\beta}$ = 14,0, $J_{2\alpha4\alpha}$ = 2,0, 2-Hα); 3,00 (1H, d, J = 14,0, 2-Hβ); 3,7...4,12 (m 5-H, 6-H)	7,12...7,25 (5H, m)	5,85 (1H, m, 4-H); 6,12 (1H, d, 3-H); J_{34} = 3,6; 2,15 (3H, c, CH_3)	2,30 br.s
IVa	1,22 t, 4,18 q	3,08 (1H, d.d.d, $J_{24\alpha}$ = 2,0, $J_{4\alpha5}$ = 12,0, $J_{4\alpha4\beta}$ = 17,0, 4-Hα); 3,20 (1H, d.d, $J_{4\alpha4\beta}$ = 17,0, $J_{54\beta}$ = 5,0, 4-Hβ); 3,72 (1H, d, J_{56} = 12,0, 6-H); 3,95 (1H, d.d.d, J_{56} = 12,0, $J_{54\beta}$ = 5,0, $J_{54\alpha}$ = 12,0, 5-H); 6,50 (1H, d, $J_{24\alpha}$ = 2,0, 2-H	6,12 (1H, d, 3-H); 6,28 (1H, d.d, 4-H); 7,30 (1H, d, 5-H); J_{34} = 4,0; J_{54} = 1,8	7,4...7,6 (5H, m)	
IVc	1,00 t, 4,05 q	2,83 (1H, d.d.d.d, $J_{4\alpha4\beta}$ = 17,5, $J_{4\alpha2}$ = 2,5, $J_{4\alpha5}$ = 7,0, J = 3,5, 4-Hα); 3,02 (1H, d.d, br. $J_{4\alpha4\beta}$ = 17,5, $J_{4\beta5}$ = 3,5, 4-Hβ); 3,77 (2H, m, 5-H, 6-H); 6,61 (1H, d, $J_{4\alpha2}$ = 2,5, 2-H)	7,3 (5H, m)	6,53 (1H, d.d, 4-H); 6,78 (1H, d, 3-H); 7,58 (1H, d, 5-H); J_{34} = 3,6, J_{45} = 2,0	
IVd	0,95 t, 3,90 q	2,67 (1H, d.d.d.d, , $J_{4\alpha4\beta}$ = 17,5, $J_{4\alpha2}$ = 2, J = 3,5, $J_{4\alpha5}$ = 7,0, 4-Hα); 2,90 (1H, d.d, br. $J_{4\alpha4\beta}$ = 17,5, $J_{4\beta5}$ = 7,0, 4-Hβ); 3,53 (2H, m, 5-H, 6-H); 6,45 (1H, d, $J_{4\alpha2}$ = 2,0, 2-H)	6,7 (2H, d, 2-H, 6-H); 7,12 (2H, d, 3-H, 5-H); J_{23} = J_{56} = 9,0; 3,66 (s, 3H, CH_3O)	6,40 (1H, d.d, 4-H); 6,67 (1H, d, 3-H); 7,43 (1H, d, 5-H); J_{34} = 4,0; J_{54} = 2,0	
IVe	1,05 t, 4,03 q	2,78 (1H, d.d.d.d, $J_{4\alpha4\beta}$ = 17,5, J = 3,5, $J_{4\alpha5}$ = 7,0, $J_{4\alpha2}$ = 2,5, 4-Hβ); 3,0 (1H, d.d, br. $J_{4\alpha4\beta}$ = 17,5, $J_{4\beta5}$ = 3,5, 4-Hβ); 3,77 (2H, m, 5-H, 6-H); 6,68 (1H, d, $J_{24\alpha}$ = 2,5, 2-H)	7,3 (5H, s)	2,35 (3H, s, CH_3); 6,16 (1H, m, 4-H); 6,56 (1H, d, 3-H); J_{34} = 3,6	
IVf	0,95 t, 3,81 q	2,83 (2H, m, 4-Hα, 4-Hβ); 3,85 (2H, m, 5-H, 6-H); 6,30 (1H, br. s, 2-H)	7,2...7,4 (3H, m, C_6H_3); 3,75 (6H, s, CH_3C)	6,5 (1H, d.d, 4-H); 6,78 (1H, d, 3-H); 7,66 (1H, d, 5-H); J_{34} = 3,6, J_{45} = 1,8	
IVg	0,92 t, 3,92 q	2,87 (2H, m, 4-Hα, 4-Hβ); 3,68 (2H, m, 5-H, 6-H); 6,16 (1H, br. s, 2-H)	7,28 (4H, m, C_6H_4)	6,50 (1H, d.d, 4-H); 6,98 (1H, d, 3-H); 7,65 (1H, d, 5-H); J_{34} = 4,0, J_{54} = 2,0	

TABLE 2. (continued)

1	2	3	4	5	6
IVh	1,10 t, 4,03 q	2,85 (1H, d.d.d, $J_{4\alpha 2}$ = 2,0, $J_{4\alpha 5}$ = 13,0, $J_{4\alpha 4\beta}$ = 18,0, 4-Hα); 3,03 (1H, d.d, $J_{4\alpha 4\beta}$ = 18,0, $J_{4\beta 5}$ = 5,0, 4-Hβ); 3,72 (1H, d, J_{56} = 13,0, 6-H); 3,90 (1H, d.d.d, J_{56} = 13,0, $J_{54\beta}$ = 5,0, $J_{54\alpha}$ = 13,0 5-H); 6,60 (1H, d, $J_{24\alpha}$ = 2,0, 2-H)	7,50 (2H, d, 2-H, 6-H); 8,20 (2H, d, 3-H, 5-H); J_{23} = 9,0, J_{56} = 9,0	6,50 (1H, d.d, 4-H); 6,75 (1H, d, 3-H); 7,03 (1H, d, 5-H); J_{34} = 4,0, J_{54} = 1,8	
IVi	1,03 t, 3,89 q	2,84 (2H, m, 4-Hα, 4-Hβ); 3,64 (2H, m, 5-H, 6-H); 6,42 (1H, d, $J_{24\alpha}$ = 2,0, 2-H)	6,73 br.s, 7,15 s, 2-H, 5-H, 6-H; 3,80 (6H, s, CH_3O)	2,30 (3H, s, 5-CH_3); 6,0 (1H, m, 4-H); 6,55 (1H, d, 3-H); J_{34} = 3,6	
IVj	1,02 t, 3,94 q	2,88 (1H, d.d.d, $J_{4\alpha 4\beta}$ = 17,0, $J_{4\alpha 5}$ = 11,0, $J_{24\alpha}$ = 2,0, 4-Hα); 3,02 (1H, d.d, $J_{4\alpha 4\beta}$ = 17,0, $J_{4\beta 5}$ = 5,5, 4-Hβ); 3,70 (1H, d.d.d, $J_{4\alpha 5}$ = 11,0, $J_{4\beta 5}$ = 5,5; J_{56} = 13,0, 5-H); 3,92 (1H, d, 6-H, J_{56} = 13,0)	7,4 (2H, d, 2-H, 6-H); 7,5 (2H, d, 3-H, 5-H); J_{23} = J_{56} = 9,0	6,24 (1H, d.q, 4-H); 6,34 (1H, d, 3-H); 2,36 (3H, br.s 5-CH_3); J_{34} = 4,0, J_{4CH_3} = 0,8	
IVk	1,12 t, 4,12 q	3,07 (2H, m, 4-Hα, 4-Hβ); 3,70 (2H, m, 5-H, 6-H); 6,43 (1H, d, $J_{4\alpha 2}$ = 2,0, 2-H)	6,03 (1H, d.d, 3-H); 6,20 (1H, d.d, 4-H); 7,27 (1H, d.d, 5-H); J_{34} = 3,6; J_{35} = 1,0; J_{45} = 2,0	7,0 (1H, d.d, 4-H); 7,27 (1H, d.d, 3-H); 7,42 (1H, d.d, 5-H); J_{34} = 4,5, J_{45} = 5,5; J_{35} = 1,2	
VIIa	1,1 t, 4,02 q	2,95 (2H, m, 4-Hα, 4-Hβ); 3,63 (2H, m, 5-H, 6-H); 6,25 (1H, d, $J_{24\alpha}$ = 2,0, 2-H)	5,83 (1H, d, 4-H); 6,03 (1H, d, 3-H); 7,08 (15H, m, $C(C_6H_5)_3$)	7,33 (5H, s)	
VIIc	0,93 t, 3,90 q	2,80 (2H, m, 4-Hα, 4-Hβ); 3,62 (2H, m, 5-H, 6-H); 6,27 (1H, d, $J_{4\alpha 2}$ = 2,0, 2-H)	7,17 (5H, m)	6,12 (1H, d, 3-H); 6,73 (1H, d, 4-H); J_{34} = 3,6; 7,20 (15H, m, $C(C_6H_5)_3$	
VIId	0,97 t, 3,92 q	2,78 (2H, m, 4-Hα, 4-Hβ); 3,57 (2H, m, 5-H, 6-H); 6,28 (1H, d, $J_{4\alpha 2}$ = 2,0, 2-H)	6,83 (2H, d, 2-H, 6-H); 7,08 (2H, d, 3-H, 5-H); J_{23} = J_{56} = 9,0; 3,68 (3H, s, CH_3O)	6,13 (1H, d, 3-H); 6,67 (1H, d, 4-H); 7,15 (15H, m, $C(C_6H_5)_3$)	

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*In all cases, for ethyl groups J = 7.0.

3-(5-Triphenyl-2-furyl)-5-phenyl-6-ethoxycarbonyl-2-cyclohexenone (VIIc). Here 0.63 g (1.8 mmole) of $TrClO_4$ was added to a solution of 0.6 g (1.88 mmole) of ketol II in 5 ml of acetonitrile. The mixture was heated to 30-40°C until the reagents totally dissolved. Turbulent crystallization began from the warm solution. The sediment was filtered off and 0.8 g of chalcone was obtained.

Compounds VIIa, d were prepared similarly. The characteristics of cyclohexanones VIIa, c, d are reported in Tables 1 and 2.

(5-Methyl-2-furyl)triphenylmethane (VIII). A mixture of 0.83 g (2.5 mole) of ketol IIb and 0.83 g (2.5 mmole) of $TrClO_4$ in 10 ml of acetonitrile was held for 2 h at room temperature, cooled, and 0.4 g (49%) of compound VIII was obtained. PMR spectrum (CD_2Cl_2); 2.20 (3H, s, CH_3); 5.80 (2H, s, 3-H, 4-H, furan); 6.79-7.30 ppm (15H, m, $C(C_6H_5)_3$). See Table 1 for the other characteristics of compound VIII.

The filtrate obtained after separation of methane VIII was evaporated, the sediment was recrystallized from ethanol, and 0.25 g (41%) of compound VI was obtained.

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