Reaction of 5-aryl-2-tosylmethylimino-2,3-dihydro-3-furanones with substituted *N*-(benzylidene)benzylamines. Crystal structure of 1-benzyl-5-*p*-methoxyphenyl-2-(*p*-chlorobenzoyl)acetylimidazole

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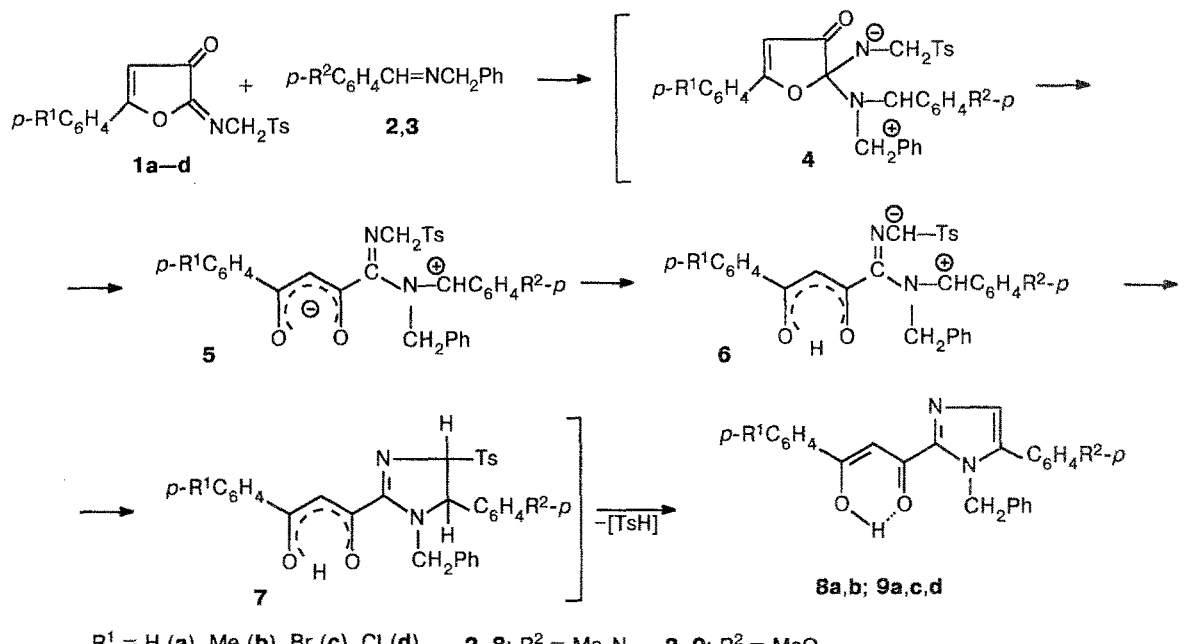
5-Aryl-2-aroylacetyl-1-benzylimidazoles were synthesized by treatment of 5-aryl-2-tosylmethylimino-2,3-dihydro-3-furanones with *N*-(benzylidene)benzylamines containing electron-donating substitutents in the benzylidene moiety. The structure of 1-benzyl-5-*p*-methoxyphenyl-2-(*p*-chlorobenzoyl)acetylimidazole was studied by X-ray diffraction.

Key words: *N*-substituted 2-imino-5-aryl-2,3-dihydro-3-furanones, recyclization, 5-aryl-2-aroylacetyl-1-benzylimidazoles, X-ray analysis.

Reactions of *N*-substituted 2-imino-2,3-dihydro-3-furanones with diphenylketene and aroylketenes yield the products of [2+2]- (see Ref. 1) and [2+4]-cycloaddition (see Ref. 2) to the C=N bond, respectively. The behavior of other classes of unsaturated compounds in this reaction has not been studied.

The purpose of the present work was to study the reaction of 5-aryl-2-tosylmethylimino-2,3-dihydro-3-furanones (**1a—d**) with *N*-(*p*-dimethylaminobenzylidene)- and *N*-(*p*-methoxybenzylidene)benzylamines (**2**, **3**). The reaction of equimolar amounts of reagents **1** with **2** or **3** unexpectedly gave 5-aryl-2-aroylacetyl-1-benzylimidazoles (**8a,b** or **9a,c,d**) as yellow crystalline compounds (Scheme 1).

Scheme 1



R^1 = H (**a**), Me (**b**), Br (**c**), Cl (**d**) **2**, **8**: $R^2 = Me_2N$ **3**, **9**: R^2 = MeO

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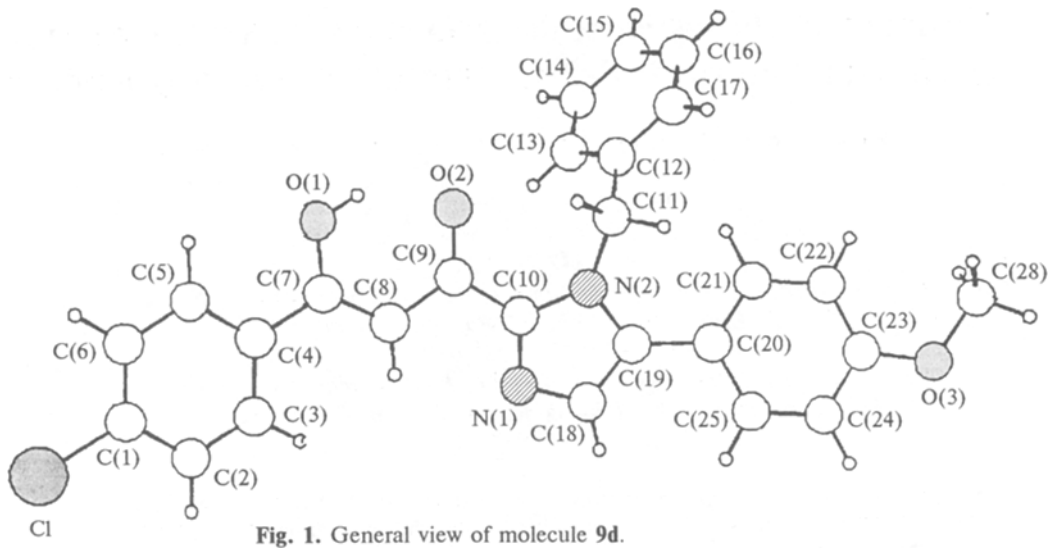
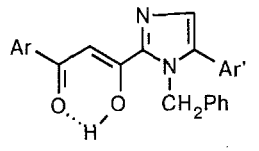


Fig. 1. General view of molecule **9d**.

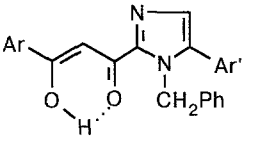
The structures of compounds **8a,b** and **9a,c,d** were confirmed by spectroscopic data. For example, the mass spectrum (EI) of imidazole **8a** contains peaks at *m/z* (I_{rel}(%)): 423 $[M]^+$ (100), 332 $[M-PhCH_2]^+$ (8), 318 $[M-PhCO]^+$ (42), 304 $[M-PhCOCH_2]^+$ (11), and 276 $[M-PhCOCH_2CO]^+$ (19). Compound **9a** was found to behave similarly under electron impact. According to the data presented, imidazoles **8** and **9** contain an aroylacetyl moiety, as is evident from the presence of ion peaks at $[ArCO]^+$, $[M-ArCO]^+$, $[M-ArCOCH_2]^+$, and $[M-ArCOCH_2CO]^+$. The IR spectra of imidazoles **8** and **9** synthesized by us contain an intense band at 1590–1600 cm^{-1}, which is typical of an enolized β-dicarbonyl moiety.[3]

In solution, the compounds synthesized also mostly exist (~95 %) in an enol form, as follows from a comparison of integral intensities of signals of vinyl protons (5.55–5.85 ppm) and CH_2 group protons of the dicarbonyl moiety (4.72–4.85 ppm) in the ^1H NMR spectra. A singlet of CH_2 protons of the benzyl group was found at 5.55–5.71 ppm, which does not contradict the literature data for substituted 1-benzylimidazoles.[4] The ^1H NMR spectrum of compound **9c** displays a broadened signal of enol group proton (15.55 ppm). We did not suceed in detecting similar signals in the spectra of compounds **8a,b** and **9a,d**, probably because of their even stronger broadening. The ^{13}C NMR spectrum of imidazole **8a** contains signals characterizing an enolized aroylacetyl moiety: 182.63 ppm (CO), 95.03 ppm (CH), and 160.05 ppm (COH). We did not find signals characterizing the dicarbonyl form of compound **8a** in its ^{13}C NMR spectrum.

Taking into account that the spectral data do not make it possible to unambiguously determine the type of enolization in the aroylacetyl moiety of compounds **8** and **9** or to choose one of the alternative structures **A** and **B**, we carried out an X-ray diffraction study of compound **9d**.



A



B

The structure of molecule **9d** is shown in Fig. 1. The imidazole moiety is planar. The distribution of bond lengths in it suggests localization of the N(1)=C(10) and C(18)=C(19) double bonds and the absence of conjugation. The bond lengths and bond angles in the molecule have usual values and do not require any discussion. The conformation of the planar O(2)—C(9)—C(8)—C(7)—O(1)—H moiety is stabilized by an intramolecular hydrogen bond O(1)—H...O(2) (2.546 Å) with the following parameters: O(1)—H(1) 0.88 Å, H(1)...O(2) 1.80 Å, the angle O(1)—H(1)—O(2) being 141.6°. The N(1)=C(10) double bond of the imidazole ring is oriented *trans* to the C(9)=O(2) carbonyl group. The plane of the O(2)—C(9)—C(8)—C(7)—O(1)—H moiety, which is coplanar with the plane of the chlorobenzene group, forms an angle of 14.1° with the imidazole ring (the torsion angle O(1)—C(9)—C(10)—N(2) is 13.1°). The orientation of the benzyl and *p*-methoxybenzene moieties relative to the imidazole ring is characterized by torsion angles of C(10)—N(2)—C(11)—C(12) −98.0° and N(2)—C(19)—C(20)—C(21) −29.3°, respectively. The crystal does not contain hydrogen bonds, other than those noted above, and another shortened intermolecular contacts.

Thus, crystalline benzoylacetylimidazoles **8** and **9** exist as forms **B** with an enolized benzoyl group.

The first step of the reaction probably involves the attack of the trigonal N atom of compound **2** or **3** at the C(2) atom of heterocycle **1** and formation of zwitterionic adduct **4**, which transforms into intermediate **5** due to C—C bond cleavage. Then, proton migration from the

Table 1. Physicochemical properties of 5-aryl-2-aroylacetyl-1-benzylimidazoles

Compound	Yield (%)	M.p.*/°C	Molecular formula	Found / Calculated (%)			
				C	H	Br(Cl)	N
8a	63	192—193	$C_{27}H_{25}N_3O_2$	76.51 76.59	6.04 5.91		9.88 9.93
8b	65	193—194	$C_{28}H_{27}N_3O_2$	76.81 76.88	6.15 6.18		9.69 9.61
9a	78	130—131	$C_{26}H_{22}N_2O_3$	76.14 76.09	5.32 5.36		6.81 6.83
9c	65	155—156	$C_{26}H_{21}BrN_2O_3$	63.88 63.80	4.18 4.29	16.40 16.36	5.78 5.72
9d	76	128—129	$C_{26}H_{21}ClN_2O_3$	70.11 70.19	4.78 4.72	7.95 7.98	6.34 6.30

* Compound **8a** was purified by recrystallization from benzene, **8b** from CCl_4, **9a,d** from methanol, and **9c** from acetonitrile.

Table 2. Spectral characteristics of 5-aryl-2-aroylacetyl-1-benzylimidazoles **8a,b** and **9a,c,d**

Compound	IR, ν/cm^{-1}, O=C—CH=C—OH	^1H NMR, δ				
		Me	$PhCH_2$	CH (CH_2, diketone)	$Ar+CH_{imidazole}$	Solvent
8a	1595	2.88(s)	5.58(s)	5.76(s)(4.71(s))	7.21(m)	$CDCl_3$
8b	1600	2.96(s) 2.38(s)	5.61(s)	5.75(s)(4.71(s))	7.16(m)	$CDCl_3$
9a	1595	3.68(s)	5.55(s)	5.65(s)(4.71(s))	7.31(m)	$CDCl_3$
9c	1590	3.75(s)	5.66(s)	5.75(s)(4.71(s))	7.25(m)	$CDCl_3$
9d	1595	3.75(s) 3.78(s)	5.65(s) 5.71(s)	5.71(s)(4.75(s)) 5.85(s)(4.85(s))	7.35(m) 7.35(m)	$CDCl_3$ DMSO-d_6

methylene group, linked to the tosyl moiety, to one of the O atoms results in intermediate **6**. The interaction between C atoms bearing opposite charges completes formation of the imidazole system in **6**, and elimination of toluenesulfinic acid yields compound **8** or **9**.

The electron-donatind substituents R^2 in *N*-(benzylidene)benzylamines **2** and **3** not only facilitate nucleophilic attack but also stabilize intermediates **4**—**6**.

Table 3. Bond lengths (*d*) and bond angles (ω) in molecule **9d**

Bond	*d*/Å	Angle	ω/deg
Cl—C(1)	1.747	C(23)—O(3)—C(26)	117.4
C(4)—C(7)	1.473	C(10)—N(2)—C(11)	126.2
O(1)—C(7)	1.331	C(11)—N(2)—C(19)	126.7
O(1)—H(1)	0.88	Cl—C(1)—C(6)	119.3
C(7)—C(8)	1.359	C(3)—C(4)—C(5)	118.6
C(8)—C(9)	1.432	C(5)—C(4)—C(7)	119.8
O(2)—C(9)	1.252	O(1)—C(7)—C(8)	121.2
C(5)—C(6)	1.387	C(7)—C(8)—C(9)	121.3
N(2)—C(10)	1.381	O(2)—C(9)—C(10)	121.6
C(13)—C(14)	1.389	N(1)—C(10)—N(2)	111.3
N(2)—C(19)	1.381	N(2)—C(10)—C(9)	126.4
C(16)—C(17)	1.375	C(11)—C(12)—C(13)	122.4
C(3)—C(26)	1.417	C(10)—N(1)—C(18)	105.2
O(3)—C(23)	1.375	C(10)—N(2)—C(19)	106.5
C(11)—C(12)	1.510	Cl—C(1)—C(2)	119.1
C(1)—C(2)	1.378	C(2)—C(1)—C(6)	121.6
C(2)—C(3)	1.375	C(3)—C(4)—C(7)	121.6
C(3)—C(4)	1.392	C(1)—C(7)—C(4)	114.3
C(4)—C(5)	1.396	C(4)—C(7)—C(8)	124.5
N(1)—C(10)	1.329	O(2)—C(9)—C(8)	122.5
C(12)—C(13)	1.370	C(8)—C(9)—C(10)	115.9
C(18)—C(19)	1.370	N(1)—C(10)—C(9)	122.4
C(15)—C(16)	1.370	N(2)—C(11)—C(12)	114.1
N(2)—C(11)	1.473	C(11)—C(12)—C(17)	119.3
C(20)—C(21)	1.385	C(13)—C(12)—C(17)	118.5
C(21)—C(22)	1.395	N(2)—C(19)—C(18)	105.2
C(22)—C(23)	1.376	C(18)—C(19)—C(20)	127.2
C(23)—C(24)	1.384	O(3)—C(23)—C(24)	115.3
C(24)—C(25)	1.371	N(1)—C(18)—C(19)	111.9
C(20)—C(21)	1.408	N(2)—C(19)—C(20)	127.6
C(9)—C(10)	1.470	O(3)—C(23)—C(22)	124.6
C(1)—C(6)	1.371	C(22)—C(23)—C(24)	120.1
N(1)—C(18)	1.353		
C(14)—C(15)	1.373		
C(19)—C(20)	1.473		
C(12)—C(17)	1.388		

Note. δ 0.002—0.005 Å; $r < 0.3$—0.5°.

Table 4. Atomic coordinates in molecule **9d**

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Cl	0.31159(5)	0.1406(20)	0.82360(0)	6.25(3)
O(1)	−0.0043(1)	0.0986(3)	0.93502(9)	3.98(5)
O(2)	−0.1712(1)	0.0663(3)	0.88633(9)	3.63(5)
O(3)	−0.7785(1)	0.1691(4)	0.5363(1)	4.62(6)
N(1)	−0.2723(1)	0.0182(4)	0.6858(1)	3.15(5)
N(2)	−0.3458(1)	0.0856(3)	0.7524(1)	2.61(5)
C(1)	0.2153(2)	0.1221(5)	0.8353(2)	3.84(7)
C(2)	0.1346(2)	0.1067(5)	0.7724(2)	4.19(8)
C(3)	0.0588(2)	0.0952(5)	0.7817(2)	3.66(7)
C(4)	0.0624(2)	0.0981(4)	0.8531(1)	2.91(6)
C(5)	0.1451(2)	0.1127(5)	0.9158(2)	3.56(7)
C(6)	0.2217(2)	0.1236(5)	0.9066(2)	4.05(8)
C(7)	−0.0185(2)	0.0867(4)	0.8636(1)	2.92(6)
C(8)	−0.1018(2)	0.0671(4)	0.8066(1)	2.94(6)
C(9)	−0.1776(2)	0.0621(4)	0.8211(1)	2.94(6)
C(10)	−0.2642(2)	0.0543(4)	0.7542(1)	2.74(6)
C(11)	−0.3615(2)	0.1517(4)	0.8156(1)	2.98(6)
C(12)	−0.3825(2)	−0.0004(4)	0.8573(1)	2.95(6)
C(13)	−0.3426(2)′	−0.1720(5)	0.8694(1)	3.40(7)
C(14)	−0.3658(2)	−0.3095(5)	0.9062(2)	4.54(9)
C(15)	−0.4281(2)	−0.2754(6)	0.9313(2)	5.22(9)
C(16)	−0.4669(2)	−0.1042(6)	0.9206(2)	5.01(9)
C(17)	−0.4443(2)	0.0322(5)	0.8842(2)	4.10(8)
C(18)	−0.3603(2)	0.0277(4)	0.6395(1)	3.27(7)
C(19)	−0.4080(2)	0.0695(4)	0.6780(1)	2.72(6)
C(20)	−0.5046(2)	0.0960(4)	0.6463(1)	2.70(6)
C(21)	−0.5541(2)	0.0637(4)	0.6850(1)	3.17(6)
C(22)	−0.6459(2)	0.0875(5)	0.6503(1)	3.45(7)
C(23)	−0.6886(2)	0.1417(4)	0.5760(2)	3.33(7)
C(24)	−0.6405(2)	0.1717(5)	0.5360(2)	3.66(7)
C(25)	−0.5502(2)	0.1506(5)	0.5703(1)	3.36(7)
C(26)	−0.8296(2)	0.1544(6)	0.5765(2)	5.37(9)
H(1)	−0.053(2)	0.084(5)	0.940(2)	6.8(9)
H(2)	0.131(2)	0.104(4)	0.723(1)	4.5(7)
H(3)	0.003(2)	0.078(4)	0.738(1)	4.3(7)
H(5)	0.151(2)	0.118(4)	0.971(1)	4.9(7)
H(6)	0.278(2)	0.135(4)	0.952(1)	4.6(7)
H(8)	−0.113(1)	0.052(4)	0.755(1)	3.3(6)
H(13)	−0.299(1)	−0.186(4)	0.833(1)	3.2(6)
H(14)	−0.333(2)	−0.419(5)	0.917(2)	5.5(8)
H(15)	−0.443(2)	−0.361(6)	0.959(2)	8(1)
H(16)	−0.510(2)	−0.082(4)	0.940(1)	5.1(8)
H(14)	−0.333(2)	−0.419(5)	0.917(2)	5.5(8)
H(17)	−0.471(2)	0.146(4)	0.875(1)	5.2(8)
H(18)	−0.383(1)	0.002(4)	0.585(1)	3.0(6)
H(21)	−0.525(1)	0.003(4)	0.739(1)	3.5(6)
H(22)	−0.676(1)	0.062(4)	0.682(1)	3.2(6)
H(24)	−0.672(1)	0.208(4)	0.482(1)	3.7(6)
H(25)	−0.519(1)	0.175(4)	0.539(1)	3.1(6)
H(11.1)	−0.413(2)	0.253(4)	0.793(1)	3.7(7)
H(11.2)	−0.307(2)	0.232(4)	0.851(1)	3.7(7)
H(26.1)	−0.805(1)	0.242(4)	0.623(2)	5.9(8)
H(26.2)	−0.891(2)	0.194(4)	0.539(2)	6.5(9)
H(26.3)	−0.829(2)	0.026(4)	0.594(2)	7(1)

Substituents located at the *para* position of the benzene ring of iminofuranone **1** do not affect considerably the reaction.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer in Vaseline oil. ^{1}H NMR spectra were measured on a Bruker WP-80 SY spectrometer (80 MHz) using HMDS as the internal standard. The ^{13}C NMR spectrum was recorded on a Bruker AC-200 spectrometer (50.32 MHz) using $SiMe_4$ as the internal standard. Mass spectra were recorded on a Varian MAT-311 A instrument with direct injection of the sample into the ion source with a 70 eV energy of the ionizing electrons. The completeness of the reactions and purity of the products were monitored by TLC on Silufol UV-254 plates in a benzene—ether system, 3 : 2.

5-Aryl-2-aroylacetyl-1-benzimidazoles (8a,b; 9a,c,d). A mixture of iminofuranone **1** (0.003 mol) and azomethine **2** or **3** (0.003 mol) was heated for 15—20 min at 60 °C in 15 mL of EtOH (compounds **8a,b**) or MeOH (compounds **9a,c,d**). After cooling the reaction mixture to 0 °C, the resulting precipitate of compounds **8** or **9** was filtered off and recrystallized. The yields, m.p., and data of elemental analyses of compounds **8a,b** and **9a,c,d** are presented in Table 1. IR and ^{1}H NMR spectral data are shown in Table 2.

X-Ray study of compound 9d. The crystals of compound **9d** are monoclinic: a = 16.878(4) Å, b = 7.223(3) Å, c = 19.863(4) Å, β = 116.7°, V = 2163.9 Å^3, Z = 4, d = 1.366 g cm^{-3}, space group $P2_1/n$. Experimental data were obtained on an Enraf Nonius CAD-4 automatic diffractometer using Mo-Kα-irradiation with a graphite monochromator. The $\omega/2\theta$-scanning was used; 2437 independent nonzero reflections with $I > 3\sigma(I)$ were recorded.

The structure was determined by a direct statistic method using the MULTAN program. Least-squares refinement was performed in an anisotropic (for hydrogen atoms, isotropic) approximation. The final divergence factor was R = 0.035 (R_W = 0.038). All calculations were performed on a PDP 4/23 computer using the SDP program.[5] The interatomic distances and bond angles are presented in Table 3, and atomic coordinates are given in Table 4.

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