Chemistry of Heterocyclic Compounds, Vol. 38, No. 4, 2002

BENZAZOLES. 2*. RELATIVE ACTIVITY OF CATALYSTS AND 4-SUBSTITUTED BENZOYL CHLORIDES IN THE ACYLATION OF BENZOTHIAZOLIN-2-ONES

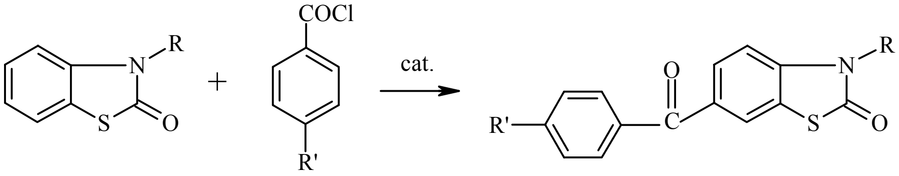
D. A. Dushamov, N. S. Mukhamedov, N. A. Aliev, Kh. M. Bobokulov, M. G. Levkovich, and N. D. Abdullaev

A series has been established for the relative activity of catalysts and 4-substituted benzoyl chlorides on acylation of benzothiazolin-2-ones with 4-substituted benzoyl chlorides in the presence of $FeCl_3$, $FeCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 12H_2O$, $ZnCl_2$, $ZnCl_2 \cdot 2H_2O$, $AlCl_3$, and iron acetylacetonate, as a function of the degree of acidity of the catalyst and the electrophilicity of the acylating agent.

Keywords: 6-aroylbenzothiazolin-2-ones, benzoyl chlorides, benzothiazolin-2-ones, Lewis acids, acylation.

Previously we showed the possibility of acylating benzothiazolin-2-ones [1] and benzoxazolin-2-ones [2,3] with aromatic acid chlorides using small quantities of $ZnCl_2$. The acylation of benzothiazolin-2-ones (**1a,b**) with 4-substituted benzoyl chlorides **2a-e** in the presence of $FeCl_3$, $FeCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 12H_2O$, $ZnCl_2$, $ZnCl_2 \cdot 2H_2O$, $AlCl_3$, and iron acetylacetonate (IAA) has been studied in the present work. The aim is to clarify the relative activity of the catalysts and 4-substituted benzoyl chlorides.

Usually in acylation reactions the progress of the process is determined by the activation of the acylating agents by the catalysts [4]. However the activity of Lewis acids, when using them in catalytic amounts in acylation reactions, differs from that in the usual reactions with equimolar and excess amounts of catalysts. The strongest Lewis acids ($AlCl_3$) form stable complexes with the reaction product and are not active in catalytic amounts [5-7]. Weaker Lewis acids prove to be better catalysts, forming rather reactive complexes with acylating agents, but giving readily decomposing complexes with the reaction product, which is evident from our data (Table 1).



1a,b **2a–e** **3a–k**

1 a R = H, **b** R = Me; **2 a** R' = H, **b** R' = Me, **c** R' = OMe, **d** R'= Br, **e** R'= NO_2; **3 a-e** R =H, **f-k** R = Me; **a**, **f** R' = H; **b**, **g** R' = Me; **c**, **h** R' = OMe; **d**, **j** R' = Br; **e**, **k** R' = NO_2

---

* For Part 1 see [1].

Institute of Plant Chemistry, Uzbek Academy of Sciences, Tashkent 700170. Translated from Khimiya Geterotsiklicheskikh Soedinenii., No. 4, pp. 503-506, April, 2002. Original article submitted November 8, 2000.

TABLE 1. Conditions of Benzoylating Benzothiazolin-2-one*

Catalyst	Dependence of yield of 6-benzoylbenzothiazolin-2one (**3a**) on time, %					
	0.5 h	1 h	1.5 h	2 h	2.5 h	3 h
$FeCl_3$	29	43	56	61	68	71
$FeCl_3·6H_2O$	26	41	53	60	67	70
$FeCl_3·12H_2O$	25	40	50	60	65	70
$ZnCl_2$	16	27	45	47	56	61
$FeCl_3·2H_2O$	15	23	43	45	53	55
$AlCl_3$	Traces	Traces	3	5	6	8
IAA	5	7	10	15	20	40

---

* The ratio of reactants **1a** to **2a** to catalyst was 1 : 1.2 : $1·10^{-2}$, temperature was 200-205°C.

The greatest catalytic activity was displayed by $FeCl_3$, and the least by $ZnCl_2$ and IAA. None of the crystallohydrates surpassed the cortresponding anhydrous metal chloride in catalytic activity.

It is probable that the rate of formation of the complex of benzoyl chloride with the catalyst in the initial stage was greater for $FeCl_3$ due to its high acidity compared with $ZnCl_2$. The lower reaction rate in the case of $ZnCl_2$ is explained by its lower complex-forming ability and the small electrophilicity of the resulting complex. The low catalytic activity of IAA in the initial stage is probably linked with the presence of an induction period for its transition into the corresponding chloride [8-10]. The lowest activity of $AlCl_3$, being a stronger Lewis acid, is caused by the stability of its complex with the reaction product [11]. Based on the above data the catalysts can be arranged in the following order of relative activity.

$$FeCl_3 > FeCl_3·6H_2O \geq FeCl_3·12H_2O > ZnCl_2 > ZnCl_2·2H_2O > IAA > AlCl_3$$

Usually the reactivity of an acylating agent grows with an increase in the electrophilicity of the latter [12-14], but the data of [15,16] indicate an inverse dependence.

Our investigations show that 4-substituted benzoyl chlorides vary in activity. From the yields of 6-aroylbenzothiazolin-2-ones (**3a-k**) (Table 2) in separate reactions carried out under identical conditions the 4-substituted benzoyl chlorides are arranged in the following order of relative reactivity: $4\text{-}O_2NC_6H_4COCl >$ $> 4\text{-}BrC_6H_4COCl > C_6H_5COCl > 4\text{-}CH_3C_6H_4COCl > 4\text{-}CH_3OC_6H_4COCl$.

As is evident from the above, on introducing an electron-withdrawing substituent (NO_2, Br) into the benzene ring of the acylating agent the yield of the corresponding compound **3** is increased, but on introducing an electron-donor (CH_3, OCH_3) it is reduced.

The structures of the compounds **3a-k** synthesized were confirmed by IR and NMR spectroscopy, and mass spectrometry, and were confirmed by data of elemental analysis.

The IR spectra of compounds **3a-k** show the characteristic absorption bands for the stretching vibrations of the carbonyl group at position 6 (1650-1670 cm^{-1}) and for the out-of-plane deformation vibrations of the CH groups of the 1,2,4-trisubstituted benzene ring (805-825 and 870-885 cm^{-1}) (Table 2).

Peaks were detected in the mass spectra of compounds **3a-k** for the molecular ions and for the fragments $[(M^+\text{-}Ar)]^+$ (A) and Ar^+ (B) formed on cleavage of the Ar–CO bond (Table 2).

The NMR spectra of compounds **3a-k** also confirmed the proposed structures. Doublets were observed for the aromatic protons at position 4 of the benzothiazolinone ring at 7.04-7.23 ppm with *ortho* constant $J = 8.38$ Hz, a doublet of doublets for H-5 at 7.65-7.77 ppm with *ortho* and *meta* constants $J = 8.40$ and $J = 1.68$ Hz respectively, and also doublets for H-7 at 7.80-7.94 ppm with *meta* constant $J = 1.68$ Hz. In the aromatic part of the spectrum of the aroyl residue there were 4 and 5 one-proton multiplets at 7.26-7.76 ppm.

TABLE 2. Physicochemical Characteristics of Compounds **3a-k**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C (ethanol)*	Mass spectrum, *m/z* (*I*, %)			IR spectrum, ν, cm^{-1}		Yield, %
		C	H	N		M$^+$	A$^+$	B$^+$	C=O	NH	
3a	$C_{14}H_9NO_2S$	—	—	—	209-211	—	—	—	—	—	68
3b	$C_{15}H_{11}NO_2S$	67.12 66.91	4.27 4.12	5.41 5.20	223-225	269 (38)	178 (100)	91 (100)	1660, 1715	3280	51
3c	$C_{15}H_{11}NO_3S$	62.92 63.15	4.08 3.89	5.09 4.91	235-236	285 (36)	178 (100)	107 (32)	1655, 1710	3290	46
3d	$C_{14}H_8BrNO_2S$	—	—	—	266-268	—	—	—	—	—	75
3e	$C_{14}H_8N_2O_4S$	55.91 56.00	2.41 2.69	9.02 9.33	241-243	300 (28)	178 (100)	122 (20)	1655, 1715	3300	82
3f	$C_{15}H_{11}NO_2S$	67.22 66.91	3.92 4.12	4.98 5.20	145-147*^{2}	269 (29)	192 (100)	77 (26)	1660, 1710	—	66
3g	$C_{16}H_{13}NO_2S$	68.03 67.84	4.76 4.62	5.19 4.94	139-141*^{2}	283 (31)	192 (100)	91 (22)	1660, 1710	—	56
3h	$C_{16}H_{13}NO_3S$	63.96 64.21	4.69 4.38	4.27 4.68	135-136*^{2}	299 (31)	192 (100)	107 (32)	1660, 1715	—	50
3j	$C_{15}H_{10}BrNO_2S$	—	—	—	131-133	—	—	—	—	—	79
3k	$C_{15}H_{10}N_2O_4S$	57.51 57.32	2.93 3.18	9.04 8.91	124-126	314 (22)	192 (100)	122 (23)	1665, 1710	—	88

---

* The mp of compounds **3a,d,j** were identical to those given in [1].

*^{2} Solvent was benzene.

Singlets were displayed for the protons of the methyl and methoxyl groups of the aroyl residue at 2.37 and 3.46 ppm respectively. The protons of the NH group were observed at low field (9.13-11.71 ppm), and of the 3-methyl group at high field (3.41-3.46 ppm).

EXPERIMENTAL

The IR spectra of the compounds investigated were recorded on a UR 20 spectrometer in KBr tablets. The NMR spectra were taken on a UNITY 400$^+$ plus (Varian) spectrometer in $CDCl_3$. The mass spectra were obtained on a MS 25-RF instrument (Kratos) with direct insertion of the sample into the ion source, the energy of the ionizing electrons was 70 eV, and ion source temperature was 250°C. The temperature of the system for introducing the sample was 200°C. A check on the progress of reactions and the homogeneity of the compounds synthesized was effected by TLC on Silufol UV 254 plates in the solvent system benzene–ethanol, 21:4, visualizing agent was $KMnO_4$ (1 g) + H_2SO_4 (4 ml) + H_2O (96 ml).

6-Benzoylbenzothiazolin-2-one (3a). A mixture of benzothiazolin-2-one (**1a**) (1.51 g, 10 mmol), benzoyl chloride (**2a**) (1.68 g, 12 mmol), and $FeCl_3{\cdot}6H_2O$ (0.027 g, 0.1 mmol) in nitrobenzene (15 ml) was heated at 200-205°C for 3 h. The solvent was steam-distilled, the residue was filtered off, washed with water, and dried. Compound **3a** (1.73 g, 68%) was obtained.

The remaining 6-aroylbenzothiazolin-2-ones (**3b-k**) were synthesized analogously. The characteristics of compounds **3a-k** are given in Table 2

REFERENCES

1. N. S. Mukhamedov, D. A. Dushamov, N. A. Aliev, Kh. M. Bobokulov, M. G. Levkovich, and N. D. Abdullaev, *Khim. Geterotsikl. Soedin.*, 380 (2002).
2. N. S. Mukhamedov, E. L. Kristallovich, V. N. Plugar', K. Giyasov, N. A. Aliev, and N. D. Abdullaev, *Khim. Geterotsikl. Soedin.*, 1136 (1994).
3. N. S. Mukhamedov, Sh. T. Taumetova, and N. A. Aliev, *Zh. Org. Khim.*, **27**, 880 (1991).
4. A. V. Orlinkov, I. S. Akhrem, and M. E. Vol'pin, *Usp. Khim.*, **60**, 1049 (1991).
5. I. N. Zemzina and I. P. Tsukervanik, *Zh. Org. Khim.*, **2**, 697 (1966).
6. N. V. Veber and I. P. Tsukervanik, *Zh. Org. Khim.*, **5**, 116 (1969).
7. M. I. Farberov, G. S. Mironov, G. N. Timoshenko, V. A. Ustinov, and Yu. A. Moskvichev, *Kinet. Katal.*, **15**, 82 (1974).
8. I. P. Tsukervanik, *Dokl. Akad. Nauk SSSR*, **120**, 27 (1958).
9. I. P. Tsukervanik, Kh. Kim, and A. S. Kurbatova, *Zh. Obshch. Khim.*, **33**, 234 (1963).
10. I. P. Tsukervanik and F. Kh. Shadieva, *Uzb. Khim. Zh.*, No. 2, 60 (1961).
11. I. P. Tsukervanik and N. V. Veber, *Dokl. Akad. Nauk SSSR*, **180**, 892 (1968).
12. E. H. Man and C. R. Hausev, *J. Org. Chem.*, **17**, 397 (1952).
13. P. J. Slootmaekers, R. Roosen, and J. Verhulst, *Bull. Soc. Chim. Belg.*, **71**, 446 (1962).
14. N. V. Veber and N. G. Sidorova, *Zh. Org. Khim.*, **7**, 1417 (1971).
15. N. M. Cullinane, S. J. Chard, and D. M. Leyshon, *J. Chem. Soc.*, 376 (1952).
16. D. P. N. Satchell, *J. Chem. Soc.*, 5404 (1961).