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Chemistry of Diazocarbonyl Compounds: XXVIII.* Reaction of Acyclic *N*-Arylsulfonylacetamides with Rh(II)-Carbenoids as a New Synthetic Route to Alkyl Acetimidoates

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Abstract—A new procedure was proposed for the synthesis of alkyl acetimidoates via alkylation of the carbonyl group in *N*-arylsulfonylacetamides with Rh(II)-carbenoids. The procedure ensures preparation in good yield of acetimidoates having a polyfunctionalized *O*-alkyl group. The obtained alkyl acetimidoates in crystal exist as *E* isomers with respect to the C=N bond and as *s-cis* conformers relative to the C–OCHRR' bond. Alkyl *N*-arylsulfonylacetimidoates react with ammonia and hydrazine hydrate to give in good yield the corresponding carboximidamides(hydrazides) via replacement of the *O*-alkyl group. Unlike structurally related compounds having simple alkyl or aryl groups on the nitrogen atom, *N*-arylsulfonylacetimidoates readily undergo hydrolysis in the presence of moisture and traces of acids.

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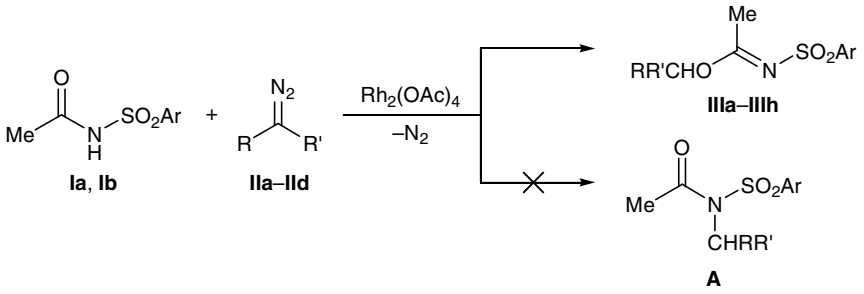
We previously found [2] that catalytic decomposition of diazo compounds in the presence of saccharin and its analogs involves exclusively O-alkylation of the carbonyl group in the heteroring with intermediate carbenoid species to give 3-oxoisothiazole 1,1-dioxide enol ethers. We thus discovered a new method for chemoselective functionalization of the carbonyl group in the sulfonimide (SO_2NHCO) fragment. The examined 3-oxoisothiazole 1,1-dioxides are cyclic analogs of known acyclic N-substituted sulfonamide derivatives which are used as antibacterial agents in medical practice and as sweeteners [3, 4]. Furthermore, some *N*-arylsulfonyl imidoates were reported to be precursors of drugs having primary sulfonamide and ester moieties [5]. Reactions of diazo compounds and intermediates derived therefrom with *N*-arylsulfonylcarboxamides were not studied previously [6]. Therefore, extension of the carbene technique for the transformation of carboxamide group into carbimidoate to acyclic *N*-arylsulfonylcarboxamides and development of a new synthetic approach to alkyl imidoates on this base seemed to be quite important and promising.

The present article reports on the results of our study on the catalytic decomposition of diazocarbonyl compounds in the presence of *N*-arylsulfonylacetamides, structure of the reaction products, and their subsequent hydrolysis and reactions with nucleophiles (ammonia and hydrazine). As substrates we used *N*-(*p*-tolylsulfonyl)- and *N*-(*p*-chlorosulfonyl)acetamides **Ia** and **Ib**. As previously [2], ketocarbenoids [7] were generated by catalytic decomposition of dimethyl diazomalonate (**IIa**), ethyl diazoacetoacetate (**IIb**), diazoacetylacetone (**IIc**), and ethyl diazoacetate (**IId**) in the presence of dirhodium tetraacetate. The reactions were carried out in methylene chloride at 18–20°C; the rhodium catalyst was taken in an amount of 0.1 to 2 mol %. When the initial diazo compound disappeared, the mixture was separated by chromatography on neutral silica gel, and the products were identified by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and X-ray analysis.

Our experiments showed that Rh(II)-ketocarbenoids generated from diazocarbonyl compounds **IIa**–**IId** reacted with *N*-sulfonylacetamides **Ia** and **Ib** to give alkyl acetimidoates **IIIa**–**IIIh** as the major products

* For communication XXVII, see [1].

Scheme 1.



I, Ar = *p*-MeC_6H_4 (a), *p*-ClC_6H_4 (**b**); **II**, R = R' = MeOCO (**a**), MeCO (**c**); R = EtOCO, R' = MeCO (**b**); R = H, R' = EtOCO (**d**); **III**, R = R' = MeOCO, Ar = *p*-MeC_6H_4 (**a**), *p*-ClC_6H_4 (**b**); R = EtOCO, R' = MeCO, Ar = *p*-MeC_6H_4 (**c**), *p*-ClC_6H_4 (**d**); R = R' = MeCO, Ar = *p*-MeC_6H_4 (**e**), *p*-ClC_6H_4 (**f**); R = H, R' = EtOCO, Ar = *p*-MeC_6H_4 (**g**), *p*-ClC_6H_4 (**h**).

(Scheme 1). No isomeric *N*-alkyl-*N*-sulfonylacetamides **A** were detected in the reaction mixtures by ^{1}H NMR spectroscopy.

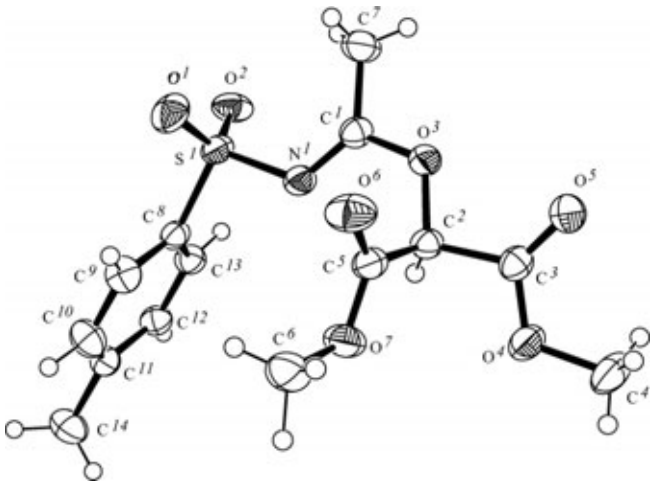
The structure of products **IIIa**–**IIIh** was determined on the basis of their ^{1}H and ^{13}C NMR spectra, as well as by comparison of their spectral parameters with those reported in [2] for the corresponding *O*-alkyl saccharin derivatives [2]. In the ^{1}H and ^{13}C NMR spectra of **IIIa** and **IIIb**, signals from the O–CH fragment appeared at δ 5.4–5.5 and δ_C 74.6–74.7 ppm, respectively (cf. δ 5.7–5.9 and δ_C 76–77 ppm for their analogs derived from 3-oxoisothiazole 1,1-dioxides [2]). The structure of compound **IIIa** was unambiguously proved by X-ray analysis. The molecule of adduct **IIIa** is shown in figure, and its principal geometric parameters (bond lengths and bond and torsion angles) are listed in table. It is seen that compound **IIIa** (and hence its analogs **IIIb**–**IIIh**) is characterized by *E* configuration at the C=N double bond and, like *O*-alkyl saccharin derivatives [2], *s-cis* conformation with respect to the C–OCHRR' bond.

As follows from the ^{1}H and ^{13}C NMR and IR data, alkyl acetimidoates **IIIc**–**IIIf** having an acetyl group in the 1,3-dicarbonyl fragment exist in solution as diketone tautomers, in contrast to the corresponding *N*-alkyl amides and lactams which exist in solution exclusively in the enol form [8].

Alkyl *N*-arylsulfonylacetimidoates **III** turned out to be very labile compounds. They readily underwent hydrolysis in the presence of traces of moisture and acids; imidoates **IIIc**–**IIIf** having an acetyl group in the OCHRR' fragment were the most sensitive to hydrolysis. For example, complete hydrolysis of compounds **IIIc** and **IIIf** with quantitative regeneration of initial amides **Ia** and **Ib** occurred during separation of the reaction mixture on silica gel (pH <6).

The reaction with methanol followed a different pattern: heating of compounds **III** in methanol resulted in formation of the corresponding arenesulfonamides **Va** and **Vb** rather than imides **I** (Scheme 2). In addition, from the reaction mixtures we isolated 2-hydroxy-1,3-dicarbonyl compounds **VIa**–**VIc**; compound **VIa** was identified by comparison with published data [9], while **VIb** and **VIc** were converted into crystalline derivatives, 1-phenyl-4-phenylhydrazono-3-methyl-4,5-dihydro-1*H*-pyrazol-5-one [10] and 3-hydroxypentane-2,4-dione bis(2,4-dinitrophenylhydrazone) [11], respectively.

Insofar as imides **I** are fairly stable in methanol solution and they do not undergo hydrolysis even on prolonged heating, arenesulfonamides **V** are formed in the methanolysis of compounds **III** from other precursors. It is known that the *O*-alkyl group in carbimidoates may be replaced by another alkyl group on heating with excess amount of the corresponding



Structure of the molecule of dimethyl [*N*-(*p*-tolylsulfonyl)-acetimidoyloxy]malonate (**IIIa**) according to the X-ray diffraction data.

Bond lengths (*d*, Å), bond angles (ω, deg), and torsion angles (φ, deg) in the molecule of dimethyl [*N*-(*p*-tolylsulfonyl)-acetimidoyloxy]malonate (**IIIa**)

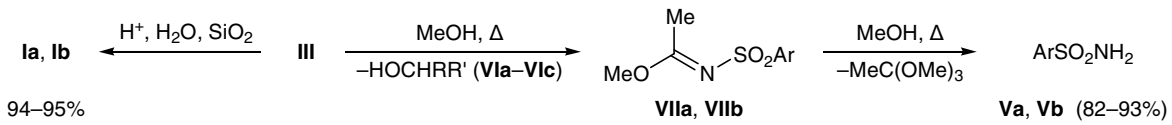
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
S^1–O^1	1.427(1)	C^2–O^3	1.426(2)	C^6–O^7	1.456(2)	C^8–C^{13}	1.386(2)
S^1–O^2	1.435(1)	C^3–O^4	1.316(2)	C^1–C^7	1.488(2)	C^9–C^{10}	1.382(2)
S^1–N^1	1.647(1)	C^4–O^4	1.453(2)	C^2–C^5	1.525(2)	C^{10}–C^{11}	1.393(2)
S^1–C^8	1.753(1)	C^3–O^5	1.190(2)	C^2–C^3	1.527(2)	C^{11}–C^{12}	1.389(2)
C^1–N^1	1.280(2)	C^5–O^6	1.193(2)	C^2–H^2	0.949(2)	C^{11}–C^{14}	1.498(2)
C^1–O^3	1.346(2)	C^5–O^7	1.313(2)	C^8–C^9	1.384(2)	C^{12}–C^{13}	1.382(2)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$O^1S^1O^2$	118.1(7)	$C^3O^4C^4$	116.2(12)	$O^3C^2H^2$	110.8(10)	$C^9C^8C^{13}$	120.9(12)
$O^1S^1N^1$	108.4(6)	$C^5O^7C^6$	115.8(13)	$C^5C^2H^2$	113.6(9)	$C^9C^8S^1$	120.3(10)
$O^2S^1N^1$	110.6(6)	$N^1C^1O^3$	118.3(12)	$C^3C^2H^2$	106.2(9)	$C^{10}C^9C^8$	118.9(12)
$O^1S^1C^8$	109.2(7)	$N^1C^1C^7$	130.5(13)	$O^5C^3O^4$	126.6(12)	$C^9C^{10}C^{11}$	121.6(13)
$O^2S^1C^8$	108.0(6)	$O^3C^2C^5$	109.7(11)	$O^5C^3C^2$	124.4(13)	$C^{12}C^{11}C^{10}$	118.1(12)
$N^1S^1C^8$	101.1(6)	$O^3C^2C^3$	105.9(10)	$O^6C^5O^7$	126.1(13)	$C^{10}C^{11}C^{14}$	121.1(13)
$C^1N^1S^1$	120.4(10)	$C^5C^2C^3$	110.2(11)	$O^6C^5C^2$	123.2(13)	$C^{12}C^{13}C^8$	119.2(12)
$C^1O^3C^2$	116.8(10)						
Angle	φ, deg	Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
$O^1S^1N^1C^1$	–77.3(12)	$C^1O^3C^2C^5$	–67.9(14)	$C^5C^2C^3O^4$	76.9(13)	$O^2S^1C^8C^9$	–151.4(11)
$O^2S^1N^1C^1$	53.7(12)	$C^1O^3C^2C^3$	173.2(10)	$C^6O^7C^5O^6$	–1.8(2)	$N^1S^1C^8C^9$	92.4(11)
$C^8S^1N^1C^1$	167.9(10)	$C^4O^4C^3O^5$	–2.0(2)	$C^6O^7C^5C^2$	177.4(13)	$O^1S^1C^8C^{13}$	154.7(10)
$S^1N^1C^1O^3$	177.1(9)	$C^4O^4C^3C^2$	179.2(12)	$O^3C^2C^5O^6$	–25.6(17)	$O^2S^1C^8C^{13}$	25.0(12)
$S^1N^1C^1C^7$	–2.0(2)	$O^3C^2C^3O^5$	16.7(18)	$C^3C^2C^5O^6$	90.7(16)	$N^1S^1C^8C^{13}$	–91.2(11)
$C^2O^3C^1N^1$	–2.1(17)	$C^5C^2C^3O^5$	–101.9(15)	$O^3C^2C^5O^7$	155.2(11)	$S^1C^8C^9C^{10}$	176.0(11)
$C^2O^3C^1C^7$	177.1(12)	$O^3C^2C^3O^4$	–164.5(10)	$O^1S^1C^8C^9$	–21.8(13)		

alcohol [12, 13]. Presumably, the process involves initial transesterification of **III** with formation of methyl acetimidoates **VII** which are then converted into arenesulfonamides **V**. In fact, methyl acetimidoate **VIIa** (prepared by independent method [14]) reacted with excess methanol to give *p*-toluenesulfonamide (**Va**) in quantitative yield.

The behavior of compounds **III** having bulky groups on the oxygen atom in the hydrolysis and methanolysis is consistent with the known data for analogous transformations of simpler compounds of the same series [12, 13, 15]. The hydrolysis of **III** in aqueous medium involves tetrahedral intermediate **B**; at pH < 3–4, cleavage of the C–OAlk bond usually occurs with formation of imides **I** and hydroxy carbonyl compounds **VI**, while the predominant process in neutral medium (pH > 4–7) is cleavage of the N–C bond in intermediate **B**, which leads to arenesulfonamides **V** and the corresponding esters **IX** (Scheme 3).

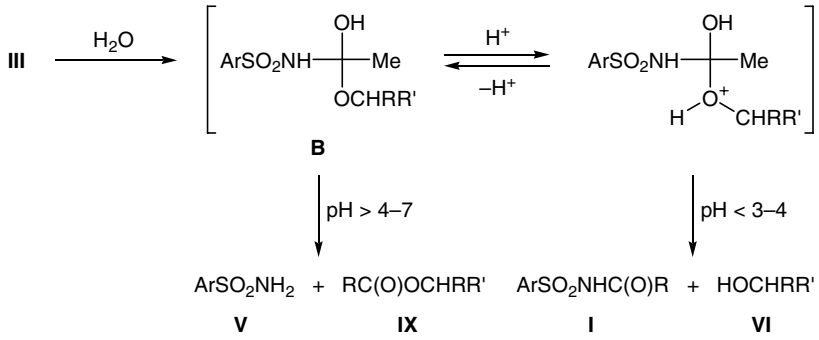
With a view to compare the reactivity of acyclic imidoates **III** with that of known analogs we examined their reactions with *p*-toluenesulfonyl isocyanate and

Scheme 2.



V, **VII**, *p*-MeC_6H_4 (**a**), *p*-ClC_6H_4 (**b**); **VI**, R = R' = MeOCO (**a**), MeCO (**c**); R = EtOCO, R' = MeCO (**b**).

Scheme 3.



nitrogen-centered nucleophiles (ammonia and hydrazine), which were repeatedly used as effective reagents in the chemistry of imidic acid esters [12, 16]. We anticipated that compounds **III** should react with *p*-toluenesulfonyl isocyanate (as the most active among the above reagents) to give [2+2]- or [4+2]-cycloaddition products or other products typical of such reactions [16]. However, compound **IIIa** failed to react with *p*-toluenesulfonyl isocyanate, though analogous reactions with known *N*-alkyl imidoates are exothermic. Likewise, no expected product was formed in the reaction of *p*-toluenesulfonyl isocyanate with methyl *N*-(*p*-tolylsulfonyl)acetimidoate (**VIIa**) having methyl group on the oxygen atom instead of the bulky O-substituent in **IIIa**. Presumably, the electron density on the nitrogen atom in molecules **III** and **VII** is considerably reduced due to the presence of a strong electron-acceptor arylsulfonyl group; therefore, nucleophilicity of the nitrogen atom is insufficient to react with such electrophiles as isocyanates under the given conditions.

Like simpler analogs [12], compound **IIIa** reacted with ammonia and hydrazine hydrate with heat evolution, and the products were amidine **Xa** and amidrazone **Xb**, respectively (Scheme 4), which were formed via replacement of the O-alkyl group. The structure of compounds **Xa** and **Xb** was confirmed by spectral data (see Experimental).

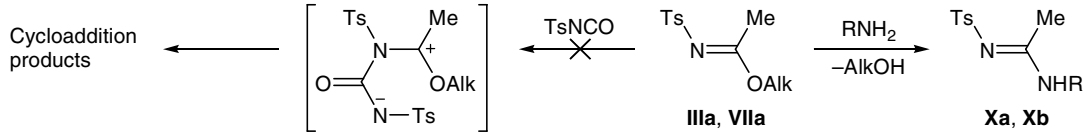
Thus we have proposed a new procedure for the synthesis of acyclic *N*-arylsulfonylacetimidoates **III** by O-alkylation of the carbonyl group in *N*-arylsulfonylacetamides with Rh(II)-carbenoids; the procedure ensures acetimidoates having polyfunctionalized groups on the oxygen atom to be obtained in good yields. Products **III** in solution and in the crystalline state are *E* isomers with respect to the C=N bond. Reactions of compounds **III** with ammonia and hydrazine hydrate give the corresponding products of replacement of the O-alkyl group in good yields. Unlike imidic acid esters having alkyl or aryl substituents on the nitrogen atom, *N*-arylsulfonyl analogs **III** readily undergo hydrolysis in the presence of atmospheric moisture and traces of acids.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 200 (200 and 50.3 MHz, respectively), Gemini 300 (300 and 75.45 MHz), Bruker Spectrospin-300 (300 and 75.46 MHz), and Bruker Spectrospin-600 (600 and 150.92 MHz) spectrometers using TMS as internal reference. The mass spectra of compounds **IIIa**–**IIIh** (electron impact, 70 eV) were obtained on a VG 12-250 quadrupole mass spectrometer (VG Instruments GmbH, Manchester Analytical) with direct sample admission into the ion source. The IR spectra were measured in KBr on an ATI Mattson Genesis Series FTIR instrument.

The X-ray diffraction data for compound **IIIa** were obtained at 213(2) K on a Siemens SMART CCD diffractometer (λ 0.71073 Å) from a 0.3×0.3×0.2-mm colorless single crystal (from benzene). Monoclinic

Scheme 4.



IIIa, Alk = $(MeOCO)_2CH$; **VIIa**, Alk = Me; **X**, R = H (**a**, 53%), NH_2 (**b**, 91%).

crystal system; unit cell parameters: a = 8.2096(15), b = 21.381(4), c = 9.2491(17) Å; β = 90.644°; V = 1623.4(5) Å^3; d = 1.405 g/cm^3; space group $P2_1/c$. Absorption coefficients were determined with the aid of SADABS program, and the structure was solved using SHELXS97 software [17].

Initial imides **Ia** and **Ib** were prepared by known procedures [18, 19] and were purified by recrystallization from methylene chloride–petroleum ether (2:1); *N*-*p*-tolylsulfonylacetamide (**Ia**), mp 135–136°C [18]; *N*-*p*-chlorophenylsulfonylacetamide (**Ib**), mp 197–198°C [19]. Diazodicarbonyl compounds **IIa**–**IIc** were synthesized and purified according to the procedures described in [2]; ethyl diazoacetate (**IId**) from Fluka was distilled just before use, bp 60°C (1 mm).

The progress of reactions was monitored by TLC on Silufol UV-254 plates. Neutral silica gel (Chemapol L, 40–100 μm, or Merck, 70–230 mesh) was used for column chromatography.

General procedure for catalytic decomposition of dimethyl diazomalonate (IIa) in the presence of *N*-arylsulfonylacetamides Ia and Ib. Dirhodium tetraacetate, 5 mg (11 μmol), was added in one portion to a solution of 2.1 mmol of imide **Ia** or **Ib** and 2.1 mmol of dimethyl diazomalonate (**IIa**) in 17 ml of methylene chloride, and the mixture was stirred until the diazo compound disappeared completely (TLC). The mixture was then subjected to chromatography on silica gel, the main fraction was evaporated, and the residue was additionally recrystallized from benzene (**IIIa**) or CH_2Cl_2–petroleum ether (10:4; **IIIb**).

Dimethyl [*N*-(*p*-tolylsulfonyl)acetimidoyloxy]-malonate (IIIa). Yield 0.64 g (90%), colorless crystals, mp 122–123°C (from CH_2Cl_2–petroleum ether). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.0 ($C_6H_4\mathbf{C}H_3$); 21.9 ($\mathbf{C}H_3C$=N); 53.7 (OCH_3); 74.6 (OCH); 127.2, 129.8, 138.3, 144.2 (C_{arom}); 164.3 (C=N); 168.3 (C=O). Found, %: C 48.97, 49.05; H 4.95, 5.09; N 4.17, 3.99; S 9.39, 9.29. $C_{14}H_{17}NO_7S$. Calculated, %: C 48.98; H 4.99; N 4.07; S 9.34.

Dimethyl [*N*-(*p*-chlorophenylsulfonyl)acetimidoyloxy]malonate (IIIb). Yield 0.66 g (87%), colorless crystals, mp 103–104°C (from CH_2Cl_2–petroleum ether). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.2 ($\mathbf{C}H_3C$=N); 53.7 (OCH_3); 74.7 (OCH); 128.6, 129.5, 139.7, 139.8 (C_{arom}); 164.1 (C=N); 172.3 (C=O). Found, %: C 43.11, 43.06; H 3.93, 3.94; N 3.85, 3.71; S 8.91, 8.79. $C_{13}H_{14}ClNO_7S$. Calculated, %: C 42.93; H 3.87; N 3.84; S 8.81.

General procedure for catalytic decomposition of ethyl diazoacetoacetate (IIb) and diazoacetylacetone (IIc) in the presence of *N*-arylsulfonylacetamides Ia and Ib. A solution of 2.4 mmol of diazocarbonyl compound **IIb** or **IIc** in 5 ml of anhydrous methylene chloride was added to a solution of 2.3 mmol of imide **Ia** or a suspension of 2.3 mmol of imide **Ib** in 10 ml of anhydrous methylene chloride, 10 mg (22 μmol) of $Rh_2(OAc)_4$ was added, and the mixture was stirred for 18–20°C until the diazo compound disappeared completely (20–40 min; TLC). In the reactions of **IIb** and **IIc** with **Ia**, the mixture was evaporated to a volume of 2–3 ml and filtered through a thin layer of silica gel (5 g), and compounds **IIIc** and **IIIe** isolated by removal of the solvent from the main fraction were analyzed by ^{1}H NMR spectroscopy and mass spectrometry.

In the reactions of **IIb** and **IIc** with **Ib**, the mixture was evaporated to a volume of 3–4 ml, the unreacted *N*-*p*-chlorophenylsulfonylacetamide (**Ib**) was filtered off, the filtrate was passed through a layer of silica gel (5 g), and compounds **IIId** and **IIIf** isolated by removal of the solvent from the main fraction were analyzed as described above.

Ethyl 3-oxo-2-[*N*-(*p*-tolylsulfonyl)acetimidoyloxy]butanoate (IIIc). Yield 0.6 g (78%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.13 t (3H, $CH_2C\mathbf{H}_3$, J = 7.0 Hz), 2.19 s (3H, CH_3), 2.37 s (3H, CH_3), 2.56 s (3H, CH_3), 4.08 q (2H, $C\mathbf{H}_2CH_3$, J = 7.0 Hz), 5.41 s (1H, OCH), 7.25 d (2H, H_{arom}, J = 8.1 Hz), 7.68 d (2H, H_{arom}, J = 8.1 Hz). Mass spectrum, m/z (I_{rel}, %): 341 (1.2) $[M]^+$, 326 (1.4), 300 (3.3), 274 (1.9), 258 (12.8), 254 (4.8), 211 (4.8), 198 (4.7), 196 (4.7), 184 (3.2), 171 (7.7), 155 (84.0), 108 (53.8), 91 (100.0), 65 (35.9), 49 (28.2).

Ethyl 2-[*N*-(*p*-chlorophenylsulfonyl)acetimidoyloxy]-3-oxobutanoate (IIId). Yield 0.56 g (68%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.17 t (3H, $CH_2C\mathbf{H}_3$, J = 7.4 Hz), 2.21 s (3H, CH_3), 2.61 s (3H, CH_3), 4.11 q (2H, $C\mathbf{H}_2CH_3$, J = 7.4 Hz), 5.38 s (1H, OCH), 7.46 d (2H, H_{arom}, J = 9.0 Hz), 7.76 d (2H, H_{arom}, J = 9.0 Hz). Mass spectrum, m/z (I_{rel}, %): 361 (3.5) $[M]^+$, 345 (7.1), 319 (16.4), 296 (7.8), 278 (40.3), 274 (20.2), 211 (77.0), 183 (61.1), 175 (19.7), 171 (22.2), 156 (19.4), 129 (36.1), 111 (25.0), 103 (16.6), 83 (99.3), 67 (66.6), 55 (42.7), 43 (100.0).

1-Acetyl-2-oxopropyl *N*-(*p*-tolylsulfonyl)acetimidoate (IIIe). Yield 0.55 g (77%), oily substance.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.14 s (6H, $COCH_3$), 2.38 s (3H, CH_3), 2.59 s (3H, CH_3), 5.40 s (1H, OCH), 7.28 d (2H, H_{arom}, J = 8.0 Hz), 7.67 d (2H, H_{arom}, J = 8.0 Hz). Mass spectrum, m/z (I_{rel}, %): 311 (1.0) $[M]^+$, 279 (1.2), 285 (1.2), 270 (16.0), 253 (2.8), 243 (7.2), 227 (15.2), 214 (15.3), 197 (6.24), 187 (8.3), 173 (12.6), 155 (20.0), 114 (19.5), 108 (13.0), 99 (4.3), 91 (69.5), 72 (32.0), 65 (26.5), 43 (100.0).

1-Acetyl-2-oxopropyl *N*-(*p*-chlorophenylsulfonyl)acetimidoate (IIIf). Yield 0.35 g (47%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.16 s (3H, CH_3), 2.64 s (3H, CH_3), 5.40 s (1H, OCH), 7.48 d (2H, H_{arom}, J = 9.0 Hz), 7.75 d (2H, H_{arom}, J = 9.0 Hz). Mass spectrum, m/z (I_{rel}, %): 331 (4.1) $[M]^+$, 290 (1.3), 272 (1.1), 253 (3.2), 248 (8.5), 214 (3.2), 175 (47.2), 159 (8.1), 153 (8.5), 141 (7.5), 128 (8.3), 111 (41.6), 75 (13.8), 43 (100.0).

Ethyl [*N*-(*p*-tolylsulfonyl)acetimidoyloxy]acetate (IIIg). A solution of 1.7 g (15 mmol) of ethyl diazoacetate (**IId**) in 30 ml of methylene chloride was added dropwise over a period of 5 h to a solution of 2.55 g (12 mmol) of imide **Ia** and 30 mg (68 μmol) of dirhodium tetraacetate in 15 ml of methylene chloride. When the reaction was complete (TLC), the catalyst was filtered off through a layer of silica gel (7 g). An analytical sample was isolated by repeated chromatography on silica gel (20 g per gram of the reaction mixture) using petroleum ether–methylene chloride as eluent. Yield 1.5 g (41%), colorless liquid. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.8 ($\mathbf{C}H_3CH_2O$); 19.6 ($\mathbf{C}H_3C$=N); 21.4 ($\mathbf{C}H_3C_6H_4$); 61.3 ($CH_3\mathbf{C}H_2O$); 63.8 (OCH); 126.6, 129.3, 138.3, 143.4 (C_{arom}); 166.5 (C=N); 172.6 (C=O). Found, %: C 52.21, 52.16; H 5.79, 5.75; N 4.65, 4.61; S 10.81, 10.74. $C_{13}H_{17}NO_5S$. Calculated, %: C 52.17; H 5.72; N 4.67; S 10.71.

Ethyl [*N*-(*p*-chlorophenylsulfonyl)acetimidoyloxy]acetate (IIIh). A solution of 0.48 g (4.2 mmol) of ethyl diazoacetate (**IId**) in 20 ml of methylene chloride was added dropwise under stirring over a period of 1 h to a suspension of 0.5 g (2.1 mmol) of imide **Ib** and 10 mg (22 μmol) of $Rh_2(OAc)_4$ in 15 ml of methylene chloride. When the reaction was complete, the mixture was treated as described above for compound **IIIg**. Yield 0.19 g (28%), colorless liquid. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.9 ($\mathbf{C}H_3CH_2O$); 19.0 ($\mathbf{C}H_3C$=N); 60.5 ($CH_3\mathbf{C}H_2O$); 63.1 (OCH); 127.2, 128.0, 138.1, 138.7 (C_{arom}); 165.4 (C=N); 172.2 (C=O). Found, %: C 45.19, 44.96; H 4.47, 4.42; N 4.31, 4.29; S 10.07, 10.14. $C_{12}H_{14}ClNO_5S$. Calculated, %: C 45.08; H 4.41; N 4.37; S 10.02.

Decomposition of diazo compounds IIb and IIc in the presence of imides Ia and Ib, followed by methanolysis of imidic acid esters IIIc–IIIf. Dirhodium tetraacetate, 15 mg (34 μmol), was added to a solution of 7.5 mmol of *N*-arylsulfonylacetamide **Ia** or **Ib** and 7.9 mmol of diazo compound **IIb** or **IIc** in 17 ml of methylene chloride, and the mixture was stirred for 1 h at 15–20°C. When the initial diazo compound disappeared (TLC), the catalyst was filtered off through a layer of silica gel (5 g), the solvent was removed from the filtrate, the residue (a yellow oily substance) was dissolved in 5 ml of methanol, and the solution was heated for 5 h under reflux. The solvent and volatile components were distilled off at 70°C under reduced pressure (1–2 mm) into a cooled trap, and the residue was recrystallized from methylene chloride–diethyl ether (5:1).

By methanolysis of compounds **IIIc–IIIf** and subsequent recrystallization of the residue we isolated the following substances (given are the initial imidic acid number, resulting sulfonamide, yield, melting point, and reference): **IIIc**, *p*-toluenesulfonamide (**Va**), 1.05 g (82%), 135–137°C [20]; **IIId**, *p*-chlorobenzenesulfonamide (**Vb**), 0.83 g (58%), 144–145°C [21]; **IIIe**, **Va**, 0.92 g (77%), 135–136°C [20]; **IIIf**, **Vb**, 0.58 g (93%), 144–145°C [21].

The condensate collected in the trap in the methanolysis of compounds **IIIc** and **IIId** was dissolved in 15 ml of methanol, 3.9 mmol of selenium(IV) oxide was added, the mixture was left to stand for 10 h at room temperature and cooled to 0°C, 15 mmol of phenylhydrazine in 5 ml of methanol was added, and the mixture was left to stand for 3 h at 18–20°C. The solvent was distilled off under reduced pressure (10–15 mm) to a volume of ~5 ml, and the red–brown precipitate of 3-methyl-1-phenyl-4-(phenylhydrazono)-4,5-dihydro-1*H*-pyrazol-5-one was filtered off. Yield 1.3 g (63%, from **IIIc**), 1.2 g (58%, from **IIId**); mp 155–156°C (from ethanol) [11]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, CH_3), 7.18–7.97 m (10H, C_6H_5), 13.58 s (1H, OH).

The condensate collected in the trap in the methanolysis of compounds **IIIe** and **IIIf** was dissolved in 15 ml of methanol, a solution of 15 mmol of 2,4-dinitrophenylhydrazine in 15 ml of methanol was added, the mixture was heated for 4 h under reflux and cooled, and the precipitate of 3-hydroxypentane-2,4-dione bis(2,4-dinitrophenylhydrazone) was filtered through a Schott filter and recrystallized from acetone or ethanol. Yield, 1.6 g (45%, from **IIIe**), 1.39 g (39%, from **IIIf**); mp 219°C (from acetone), 217°C

(from ethanol) [10]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.15 s (6H, CH_3), 4.9 d (1H, OCH, J = 9.0 Hz), 6.3 d (1H, OH, J = 9.0 Hz), 7.94–8.91 m (6H, H_{arom}), 10.9 s (2H, NH).

Methyl *N*-(*p*-tolylsulfonyl)acetimidoate (VIIa). A mixture of 1.36 g (8 mmol) of imide **Ia** and 2.3 g (19 mmol) of trimethyl orthoacetate was heated for 2 h at 100°C. It was then cooled, the solvent and excess trimethyl orthoacetate were distilled off under reduced pressure (1–2 mm) at 18–20°C, and the residue was recrystallized from hexane. Yield 1.6 g (88%), mp 74–75°C (from hexane) [5].

A solution of 1 g (4.4 mmol) of ester **VIIa** in 10 ml of methanol was heated for 2 h under reflux, the mixture was cooled to room temperature, volatile components were distilled off under reduced pressure (1–2 mm) at 18–20°C, and the residue was recrystallized from methylene chloride–petroleum ether (4:1). Yield of sulfonamide **Va** 0.7 g (93%), mp 135–136°C [20].

***N*-(*p*-Tolylsulfonyl)acetimidamide (Xa).** Compound **IIIa**, 0.206 g (0.6 mmol), was dissolved in 3 ml of acetone, 0.15 ml of 25% aqueous ammonia was added, and the mixture was vigorously shaken (the mixture slightly warmed up). After 15 min, the solvent and excess ammonia were removed under reduced pressure, and the solid residue was washed with diethyl ether and recrystallized from ethanol. Yield 0.05 g (39%), colorless crystals, mp 144–145°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.10 s (3H, Me), 2.41 s (3H, Me), 7.30 d (2H, J = 8.0 Hz), 7.77 d (2H, J = 8.0 Hz), 7.88 br.s (2H, NH_2). Mass spectrum, m/z (I_{rel}, %): 212 (12) $[M]^+$, 155 (2), 148 (11), 107 (15), 105 (14), 91 (100), 65 (32), 63 (8), 42 (22), 39 (16).

The ether washings were evaporated under reduced pressure (15–20 mm) at room temperature to obtain a colorless crystalline substance which was identified as dimethyl 2-hydroxymalonate (**VIa**). Yield 0.70 g (79%), mp 50–52°C [9]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 s (6H, OMe), 4.76 s (1H, CH), 5.31 s (1H, OH).

***N*-(*p*-Tolylsulfonyl)acetimidohydrazide (Xb).** A solution of 0.132 g (2.64 mmol) of hydrazine hydrate in 4 ml of diethyl ether was added under continuous stirring to a suspension of 0.412 g (1.2 mmol) of compound **IIIa** in 6 ml of diethyl ether, and the mixture was stirred at 18–20°C until ester **IIIa** disappeared (~1 h, TLC). The precipitate was filtered off, washed with diethyl ether, and dried under reduced pressure (1–2 mm) at 20–25°C. Yield 0.25 g (91%), yellow crystals, mp 164–165°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.28 s (3H, Me), 2.40 s (3H, Me), 7.36 d (2H, J = 8.0 Hz), 7.78 d (2H, J = 8.0 Hz), 10.7 br.s. Mass spectrum, m/z (I_{rel}, %): 227 (10) $[M]^+$, 196 (4), 186 (6), 171 (4), 155 (33), 122 (7), 107 (4), 91 (100), 72 (17), 65 (26).

REFERENCES

1. Zakharova, V.M., Hennig, L., and Nikolaev, V.A., *Synthesis*, 2005, p. 2871.
2. Schulze, B., Nikolaev, Vs.V., Hennig, L., Rodina, L.L., Sieler, J., and Nikolaev, V.A., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 740.
3. Northey, E.H., *The Sulfonamides and Allied Compounds*, Hamor, W.A., Ed., New York: Reinhold, 1948; Mashkovskii, M.D., *Lekarstvennye preparaty* (Drugs), Moscow: Novaya Volna, 2000, vol. 2, pp. 17, 273.
4. Dorn, H., Hilgetag, G., and Rieche, A., *Angew. Chem.*, 1961, vol. 73, p. 560; Houlsby, R.D., Ghajar, M., and Chavez, L., *J. Pharm. Sci.*, 1983, vol. 72, no. 12, p. 1401.
5. Bundgaard, H. and Larsen, J.D., *J. Med. Chem.*, 1988, vol. 31, p. 2066.
6. Schulze, B., Nikolaev, Vs.V., Selivanova, A.V., and Nikolaev, V.A., Abstracts of Papers, *VIIth Conf. on the Chemistry of Carbenes*, Kazan, 2003, p. 38.
7. Doyle, M.P., McKervey, M.A., and Ye, T., *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, New York: Wiley, 1998.
8. Hrytsak, M. and Durst, T., *Heterocycles*, 1987, vol. 26, p. 2393; Brooks, G., Howarth, T.T., and Hunt, E., *J. Chem. Soc., Chem. Commun.*, 1981, p. 642; Bagley, M.C., Buck, R.T., Hind, S.L., Moody, C.J., and Slawin, A.M.Z., *Synlett*, 1996, p. 825.
9. Bak, B., *Justus Liebigs Ann. Chem.*, 1939, vol. 537, p. 286; Fisher, H.L. and Simons, H.L., *J. Am. Chem. Soc.*, 1921, vol. 43, p. 628.
10. Bome, H. and Schneider, H., *Chem. Ber.*, 1958, vol. 91, p. 988.
11. Hesse, G. and Stahl, H., *Chem. Ber.*, 1956, vol. 89, p. 2414; Bome, H. and Schneider, H., *Chem. Ber.*, 1958, vol. 91, p. 1100.
12. Neilson, D.G., *The Chemistry of Amidines and Imidates*, Patai, S. and Rappoport, Z., Eds., Chichester: Wiley, 1991, vol. 2, p. 385.
13. Dubina, V.L., Burmistrov, S.I., Ishchuk, Ya.N., and Emel'yanova, V.S., *Zh. Org. Khim.*, 1969, vol. 5, p. 236; Suzuki, O., Inoue, S., and Sato, K., *Bull. Chem. Soc. Jpn.*, 1989, vol. 62, p. 239.
14. Loev, B. and Kormendy, M.F., *Can. J. Chem.*, 1964, vol. 42, p. 176.
15. Lee, Y.-N. and Schmir, G.L., *J. Am. Chem. Soc.*, 1979, vol. 101, p. 6277.

16. Aue, D.H. and Thomas, D., *J. Org. Chem*., 1975, vol. 40, p. 2356; Vilsmaier, E. and Schneider, R., *Synthesis*, 1979, p. 293; Vilsmaier, E., Dittrich, K.H., and Sprugel, W., *Tetrahedron Lett*., 1974, p. 3601; Vilsmaier, E., Bayer, R., Laengenfelder, I., and Welz, U., *Chem. Ber*., 1978, vol. 111, p. 1136.

17. Sheldrick, G.M., *Acta Crystallogr., Sect. A*, 1990, vol. 46, p. 467; Sheldrick, G.M., SADABS: *Program for Scaling and Correction of Area Detector Data*, Göttingen: Univ. of Göttingen, Germany, 1997.

18. Chaplin, H.O. and Hunter, L., *J. Chem. Soc*., 1937, p. 1114.

19. Brans, R. and Cremlyn, R.J.W., *J. Chem. Soc. C*, 1970, p. 225.

20. Wolkow, A., *Z. Chem*., 1870, vol. VI, p. 321; *Beilsteins Handbuch der organischen Chemie*, 1928, vol. XI, p. 104.

21. Otto, R. and Brummer, L., *Justus Liebigs Ann. Chem*., 1867, vol. 143, p. 100; *Beilsteins Handbuch der organischen Chemie*, 1928, vol. XI, p. 55.