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Reactions of α-Halo Ketones with 5-Benzyl- and 5-Phenoxymethyl-2*H*,3*H*-1,3,4-oxadiazole-2-thiones

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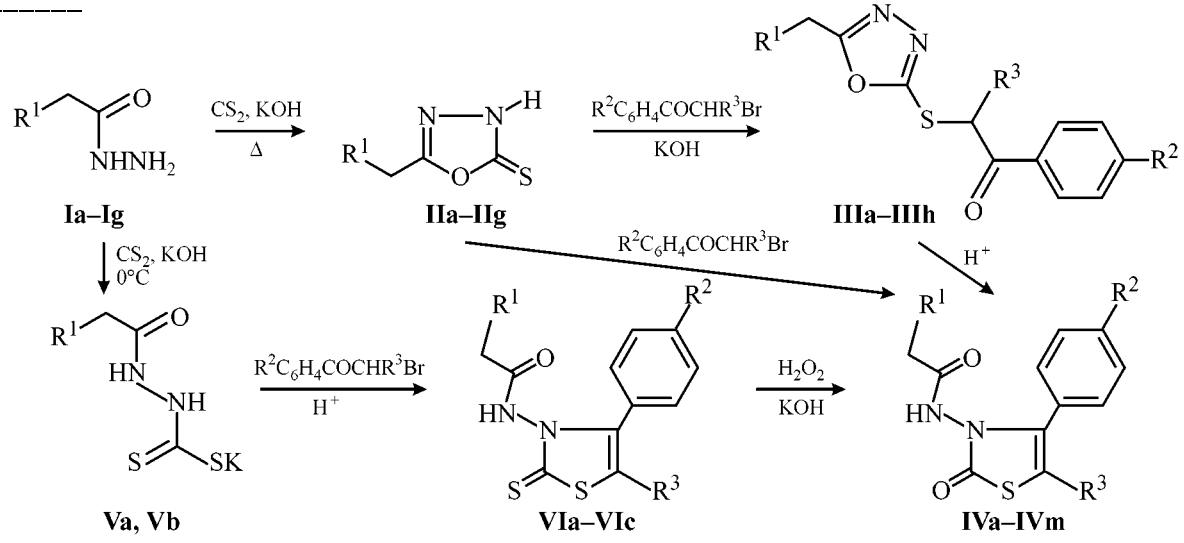
Abstract—Alkylation of 5-substituted 2*H*,3*H*-1,3,4-oxadiazole-3-thiones with α-bromo ketones in alkaline solutions yields 5-substituted 2-aroylmethylthio-1,3,4-oxadiazoles; in acidic solutions these compounds rearrange into 4-aryl-3-arylacetamido-2*H*,3*H*-1,3-thiazol-2-ones.

It is known that carboxylic acid hydrazides **I** react with CS_2 in alkaline solutions to give 5-*R*-2*H*,3*H*-1,3,4-oxadiazole-2-thiones **II**, which react with α-halo ketones in alkaline solutions to form the corresponding *S*-substituted compounds **III** [1–3]. We found that the reaction pathway and the structure of the products are largely influenced by pH, nature of the 5-substituent in the substrate, and temperature. For example, oxadiazoles **IIa**–**IIg**, when heated in alkaline solutions with α-phenacyl bromides, yield 5-substituted 2-aroylmethylthio-1,3,4-oxadiazoles **IIIa**–**IIIh**, whereas in acidic solutions the rearrangement products, 4-aryl-3-arylacetamido-2*H*,3*H*-1,3-thiazol-2-ones **IVa**–**IVm**, were obtained.

The structures of the rearrangement products was proved by independent synthesis, and that of **IVb**, by single crystal X-ray diffraction. For example, reaction of potassium (*N*-phenylacethydrazido)formodithioates **Va** and **Vb** with α-halo ketones yielded 4-aryl-3-arylacetamido-2*H*,3*H*-1,3-thiazole-2-thiones **VIa**–**VIc**. These compounds, as shown in [4, 5], when treated with hydrogen peroxide, transform into compounds **IVb**, **IVc**, and **IVf**. The ^{1}H NMR and IR spectra of the compounds obtained by different methods are identical. The yields, constants, elemental analyses, and IR and ^{1}H NMR spectra of **III**, **IV**, and **VI** are listed in Tables 1 and 2.



I, **II**, **V**, R^1 = C_6H_5 (**a**), 4-$CH_3OC_6H_4$ (**b**), 4-$C_2H_5OC_6H_4$ (**c**), 2,4-$Cl_2C_6H_3O$ (**d**), 4-BrC_6H_4O (**e**), 4-$CH_3OC_6H_4O$ (**f**), 5-phenyl-2*H*-1,2,3,4-tetrazolyl (**g**). **III**, R^1 = C_6H_5 (**a**–**d**), 4-$CH_3OC_6H_4$ (**e, f**), 4-$C_2H_5OC_6H_4$ (**g**), 2,4-$Cl_2C_6H_3O$ (**h**); R^2 = F (**a**, **h**), Cl (**b**, **g**), Br (**c**, **f**), CH_3O (**d**), H (**e**); R^3 = H (**a**–**h**). **IV**, R^1 = C_6H_5 (**a**–**d**, **i**), 4-$CH_3OC_6H_4$ (**e**, **f**), 4-$C_2H_5OC_6H_4$ (**g**), 2,4-$Cl_2C_6H_3O$ (**h**, **j**), 4-BrC_6H_4O (**k**), 4-$CH_3OC_6H_4O$ (**l**), 5-phenyl-2*H*-1,2,3,4-tetrazolyl (**m**); R^2 = F (**a**, **h**), Cl (**b**, **g**, **m**), Br (**c**, **f**, **k**, **l**), CH_3O (**d**), H (**e**, **i**); R^3 = H (**a**–**e**, **h**–**m**), CH_3 (**g**). **VI**, R^1 = C_6H_5 (**a**, **b**), 4-$CH_3OC_6H_4$ (**c**); R^2 = Cl (**a**), Br (**b**, **c**); R^3 = H (**a**–**c**).

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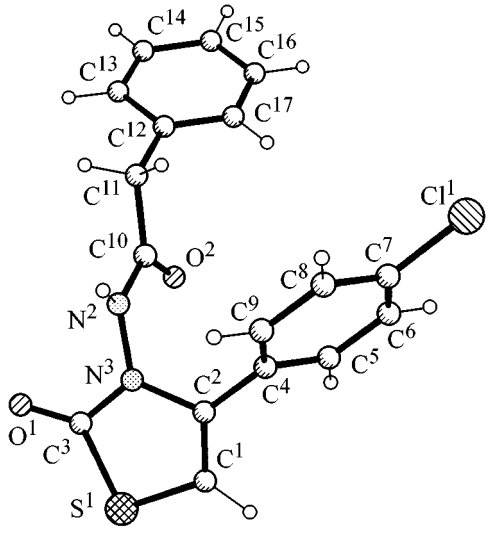
Table 1. Yields, constants, and elemental analyses of heterocyclic compounds **IIIa**–**IIIh**, **IVa**–**IVm**, and **VIa**–**VIc**

Comp. no.	Yield, %[a]	mp, °C	Found, %		Formula	Calculated, %	
			N	S		N	S
IIIa	78	124–125	8.43	9.68	$C_{17}H_{13}FN_2O_2S$	8.49	9.71
IIIb	69	106–107	8.09	9.26	$C_{17}H_{13}ClN_2O_2S$	8.12	9.30
IIIc	74	120–121	7.15	8.22	$C_{17}H_{13}BrN_2O_2S$	7.20	8.24
IIId	74	123–124	8.19	9.37	$C_{18}H_{16}N_2O_3S$	8.23	9.42
IIIe	68	116–117	8.18	9.36	$C_{18}H_{16}N_2O_3S$	8.23	9.42
IIIf	73	130–130.5	6.65	7.62	$C_{18}H_{15}BrN_2O_3S$	6.68	7.65
IIIg	70	98–99	7.17	8.21	$C_{19}H_{17}ClN_2O_3S$	7.20	8.24
IIIh	82	129–131	6.75	7.74	$C_{17}H_{11}Cl_2FN_2O_3S$	6.78	7.76
IVa	78, 80	158–159	8.50	9.78	$C_{17}H_{13}FN_2O_2S$	8.53	9.76
IVb	80, 82, 72	220–221	8.08	9.34	$C_{17}H_{13}ClN_2O_2S$	8.12	9.30
IVc	86, 85, 75	241–242	7.24	8.25	$C_{17}H_{13}BrN_2O_2S$	7.20	8.24
IVd	62, 70	176–177	8.18	9.40	$C_{18}H_{16}N_2O_3S$	8.23	9.42
IVe	68, 76	143–144	8.21	9.43	$C_{18}H_{16}N_2O_3S$	8.23	9.42
IVf	80, 85, 77	164–165	6.65	7.68	$C_{18}H_{15}BrN_2O_3S$	6.68	7.65
IVg	76, 79	149–150	7.24	8.29	$C_{19}H_{17}ClN_2O_3S$	7.20	8.24
IVh	78, 81	217–218	6.73	7.78	$C_{17}H_{11}Cl_2FN_2O_3S$	6.78	7.76
IVi	79	185–186	8.59	9.91	$C_{18}H_{16}N_2O_2S$	8.64	9.88
IVj	82	241–242	5.73	6.63	$C_{17}H_{12}Br_2N_2O_3S$	5.79	6.62
IVk	85	227–228	5.87	6.72	$C_{17}H_{11}BrCl_2N_2O_3S$	5.91	6.76
IVl	82	212–213	6.45	7.39	$C_{18}H_{15}BrN_2O_4S$	6.44	7.37
IVm	75	214–215	20.44	7.72	$C_{18}H_{13}ClN_6O_2S$	20.38	7.77
VIa	62	209.5–211	7.71	17.84	$C_{17}H_{13}ClN_2OS_2$	7.76	17.82
VIb	74	228–229	6.90	15.87	$C_{17}H_{13}BrN_2OS_2$	6.91	15.83
VIc	71	198–199	6.45	14.78	$C_{18}H_{15}BrN_2O_2S_2$	6.43	14.75

[a] Yields of compounds **IV** are given for synthesis procedures *a*, *b*, and *c*, respectively.

The structures of the synthesized compounds were proved by ^{1}H NMR and IR spectroscopy. For example, the IR spectra of compounds **III** contain characteristic absorption bands of the stretching vibrations ν(C=O) at 1670–1690 cm^{-1} and ν(C=N) at 1590–1640 cm^{-1}. In the spectra of compounds **IV** and **VI** the NH stretching vibrations are observed at 2990–3030 and 3190–3240 cm^{-1} (Table 2). The ^{1}H NMR spectra of oxadiazoles **III** contain, along with signals of the aromatic protons, also two-proton singlets of the methylene groups of the benzyl (δ 4.15–4.24 ppm) or phenoxymethyl (δ 4.95 ppm) fragment. The two-proton singlets of the methylene groups of the phenacyl residues are observed at δ 4.99–5.21 ppm, which suggests existence of these compounds in the open tautomeric form [6]. The ^{1}H NMR spectra of **IV** and **VI** contain a singlet of the methine proton of the thiazole ring at δ 6.58–7.31 ppm and an NH signal at δ 10.9–11.6 ppm (Table 2).

The structure of **IVb** was proved by single crystal X-ray diffraction. The general view of the molecule is shown in the figure, and its selected geometric parameters are listed in Table 3.



General view of the molecule of 4-(4-chlorophenyl)-3-phenylacetamido-2*H*,3*H*-1,3-thiazol-2-one (**IVb**).

Table 2. IR and ^{1}H NMR spectra of **IIIa**–**IIIh**, **IVa**–**IVm**, and **VIa**–**VIc**

Comp. no.	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum, δ, ppm				
	ν(CO)	ν(CN)	ν(NH)	R^1CH_2	$SCHR^3$	NH	ArH, m	other signals
IIIa	1690	1640		4.24 s	5.05 s (2H)		7.29–8.11 (9H)	
IIIb	1670	1580		4.24 s	5.03 s (2H)		7.29–8.01 (9H)	
IIIc	1674	1610		4.24 s	5.04 s (2H)		7.31–7.96 (9H)	
IIId	1678	1590		4.24 s	4.99 s (2H)		7.06–8.01 (9H)	3.86 s (3H, OCH_3)
IIIe	1672	1610		4.15 s	5.04 s (2H)		6.84–8.05 (9H)	3.73 s (3H, OCH_3)
IIIf	1670	1590		4.16 s	5.03 s (2H)		6.87–7.98 (8H)	3.73 s (3H, OCH_3)
IIIg	1670	1592		4.15 s	5.04 s (2H)		6.82–7.83 (8H)	3.95 q (2H, CH_2), 1.31 t (3H, CH_3)
IIIh	1678	1610		4.95 s	5.21 s (2H)		6.78–7.65 (7H)	
IVa	1690, 1710	1620	3020, 3192	3.48 s	6.58 s (1H)	11.1	7.04–7.38 (9H)	
IVb	1688, 1712	1620	3020, 3192	3.49 q	6.66 s (1H)	11.2	7.11–7.39 (9H)	
IVc	1680, 1705	1600	3020, 3190	3.48 q	6.66 s (1H)	11.2	7.03–7.55 (9H)	
IVd	1680, 1692	1610	3020, 3200	3.48 q	6.46 s (1H)	11.0	6.88–7.33 (9H)	3.78 s (3H, OCH_3)
IVe	1684, 1698	1620	3010, 3198	3.41 s	6.59 s (1H)	11.0	6.76–7.48 (9H)	3.72 s (3H, OCH_3)
IVf	1690, 1710	1618	3008, 3200	3.39 q	6.66 s (1H)	11.1	6.75–7.52 (8H)	3.73 s (3H, OCH_3)
IVg	1688, 1710	1640	2990, 3240	3.42 q	6.65 s (1H)	11.1	6.78–7.41 (8H)	3.98 q (2H, CH_2), 1.32 t (3H, CH_3)
IVh	1690, 1708	1620	3018, 3220	4.81 q	6.64 s (1H)	11.2	6.72–7.58 (7H)	
IVi	1690, 1710	1638	3030, 3200	3.38 q	2.05 s (3H)	10.9	6.92–7.45 (10H)	
IVj	1688, 1710	1620	3020, 3190	4.68 q	6.71 s (1H)	11.3	6.79–7.61 (8H)	
IVk	1694, 1710	1618	3020, 3240	4.80 q	6.70 s (1H)	11.2	6.72–7.65 (7H)	
IVl	1692, 1708	1620	3020, 3220	4.58 q	6.75 s (1H)	11.2	6.78–8.01 (8H)	3.71 s (3H, OCH_3)
IVm	1680, 1690	1610	3020, 3200	5.76 q	6.72 s (1H)	11.6	7.40–8.10 (9H)	
VIa	1690	1618	3020, 3200	3.42 q	7.14 s (1H)	11.6	7.14–7.40 (9H)	
VIb	1690	1620	3020, 3200	3.51 q	7.17 s (1H)	11.6	7.06–7.55 (9H)	
VIc	1690	1620	3020, 3198	3.39 q	7.31 s (1H)	11.6	6.78–7.82 (8H)	3.74 s (3H, OCH_3)

Table 3. Selected bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of **IVb**

Bond	*d*	Angle	ω	Bond	*d*	Angle	ω
Cl^1–C^7	1.729(6)	$C^1S^1C^3$	91.6(3)	N^1–C^2	1.410(6)	$C^1C^2C^4$	129.3(5)
S^1–C^1	1.727(6)	$N^2N^1C^3$	119.5(3)	N^2–C^{10}	1.333(6)	$N^1C^2C^4$	119.3(5)
S^1–C^3	1.770(7)	$N^2N^1C^2$	122.6(4)	C^1–C^2	1.319(7)	$O^1C^3N^1$	126.5(6)
O^1–C^3	1.194(6)	$C^3N^1C^2$	116.3(5)	C^{10}–C^{11}	1.493(7)	$S^1C^3O^1$	126.7(5)
O^2–C^{10}	1.224(5)	$C^{10}N^2N^1$	120.6(5)	C^{11}–C^{12}	1.481(8)	$S^1C^3N^1$	106.8(5)
N^1–N^2	1.375(6)	$S^1C^1C^2$	113.7(4)			$O^2C^{10}N^2$	120.2(5)
N^1–C^3	1.383(7)	$N^1C^2C^1$	111.4(5)			$O^2C^{10}C^{11}$	125.2(5)
						$N^2C^{10}C^{11}$	114.6(5)

The thiazoline ring $S^1N^1C^{1-3}$ is planar within 0.026(3) Å, and the O^1, N^2, and C^4 atoms deviate from this plane by 0.072(8), 0.183(7), and 0.044(8) Å, respectively. The geometry of this ring is usual. As in other thiazoline systems [7–9], in the molecule of **IVb** the S^1–C^1 bond [1.727(6) Å] is somewhat shorter than the S^1–C^3 bond [1.770(7) Å], and the length of the formally ordinary N^1–C^3 bond [1.383(7) Å], owing to the $n(N^1)$–$\pi^*(C^3{=}O^1)$ conjugation, is noticeably smaller than the common values for N(sp^2)–C(sp^2) bonds (1.43–1.45 Å) [10, 11]. Similarly, the $n(N^2)$–$\pi^*(C^{10}{=}O^2)$ conjugation results in shorten-

ing of the N^2–C^{10} bond to 1.333(6) Å. The N^1 and N^2 atoms have a practically trigonal planar configuration, with the bond angle sums amounting to 358.4° and 358.6°, respectively. Owing to steric interactions, the benzene ring C^{4-9} is turned by 55.0° relative to the thiazoline ring plane. The $N^1N^2C^{10}H^{2N}$ is almost orthogonal to the thiazoline ring (the corresponding dihedral angle is 81.6°), which may be due not only to steric interactions, but also to repulsion between the lone electron pairs of the N^1 and N^2 atoms. In the crystal of **IVb**, the molecules are linked in infinite chains by fairly strong [12, 13] intermolecular hydrogen bonds N^2–$H^{2N}\cdots O^2$. The main geometric parameters of these hydrogen bonds are as follows: $N^2\cdots O^2$ 2.766(5), N^2–H^{2N} 0.76(4), $H^{2N}\cdots O^2$ 2.035(4) Å; $N^2H^{2N}O^2$ angle 165.6(3)°.

EXPERIMENTAL

The IR spectra of **III**, **IV**, and **VI** (KBr pellets) were taken on a UR-20 spectrophotometer. The ^{1}H NMR spectra were measured on a Bruker-300 spectrometer with a working frequency of 300 MHz (solutions in DMSO-d_6, internal reference TMS). The mass spectra were recorded on a Varian MAT-311A spectrometer.

Single crystal X-ray diffraction study of **IVb** was performed at room temperature on an Enraf–Nonius CAD-4 automatic four-circle diffractometer (MoK_α radiation, graphite monochromator, scanning rate ratio $\omega/2\theta$ 1.2, θ_{max} 22°, sphere segment $0 \le h \le 15$, $0 \le k \le 12$, $-10 \le l \le 10$). The unit cell parameters and the orientation matrix of the crystal of **IVb** (0.2 × 0.3 × 0.55 mm) were determined from 22 reflections with $12° < \theta < 13°$. A total of 2082 reflections were measured, including 1991 unique reflections (averaging R factor 0.029). Crystal data: monoclinic, a 14.557(3), b 11.759(2), c 9.690(2) Å; β 100.48(3)°, V 1631.0(6) Å^3, Z 4, d_{calc} 1.40 g cm^{-3}, μ 0.372 mm^{-1}, F(000) 712, space group $P2_1/c$ (no. 14). The structure was solved by the direct method and refined by full-matrix least-squares in the anisotropic approximation using the SHELXS and SHELXL 93 programs [14, 15]. In the refinement we used 1267 reflections with $I > 2\sigma(I)$ {212 refined parameters, 5.98 reflections per parameter, weight scheme $\omega = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.2635P]$, $P = (F_o^2 + 2F_c^2)/3$, ratio of the maximal/average shift to the error in the last cycle 0.024/0.002)}. Correction was made for anomalous scattering; corrections for absorption were not introduced. All hydrogen atoms were revealed and refined with fixed positional and thermal parameters U_{iso} = 0.08 Å^2 (except the H^{2N} atom involved in a chain of hydrogen bonds and refined isotropically). The structure was refined to $R1(F)$ 0.0618 and $R_W(F^2)$ 0.1360, *GOF* 1.087. The residual electron density from the differential Fourier series was 0.20 and –0.23 e/Å^3. The atomic coordinates are listed in Table 4.

Table 4. Atomic coordinates (×10^4) and their equivalent isotropic thermal parameters U_{eq} (Å^2 × 10^3) in the molecule of **IVb**

Atom	x	y	z	U_{eq}
Cl^1	1644(2)	7331(1)	3937(2)	110(1)
S^1	786(1)	194(1)	3695(2)	68(1)
O^1	2545(3)	–240(3)	3460(4)	72(1)
O^2	3134(2)	2280(3)	5860(4)	61(1)
N^1	2061(3)	1624(4)	3478(4)	44(1)
N^2	2939(3)	2081(4)	3550(5)	47(1)
C^1	563(4)	1632(5)	3789(6)	60(2)
C^2	1284(4)	2281(5)	3668(5)	47(1)
C^3	1958(5)	456(5)	3530(5)	54(2)
C^4	1363(4)	3524(4)	3715(6)	47(1)
C^5	1138(4)	4120(5)	4839(6)	61(2)
C^6	1226(5)	5290(5)	4923(7)	72(2)
C^7	1527(4)	5868(5)	3856(7)	66(2)
C^8	1734(4)	5288(5)	2707(7)	68(2)
C^9	1656(4)	4129(5)	2642(6)	55(2)
C^{10}	3424(4)	2447(4)	4769(5)	44(1)
C^{11}	4294(4)	3085(6)	4653(6)	74(2)
C^{12}	4844(5)	3487(7)	6003(7)	75(2)
C^{13}	5658(6)	2955(9)	6576(9)	108(3)
C^{14}	6152(7)	3329(14)	7816(13)	172(6)
C^{15}	5866(12)	4245(17)	8474(14)	198(12)
C^{16}	5070(12)	4742(11)	7920(12)	170(7)
C^{17}	4557(7)	4371(7)	6685(8)	103(3)
H^{2N}	3087(24)	2249(29)	2868(41)	1(11)

5-Substituted 2-aroylmethylthio-1,3,4-oxadiazoles IIIa–IIIh. A solution of 10 mmol of α-halo ketone in 20 ml of ethanol was added to a solution of 10 mmol of oxadiazole **IIa**–**IIg** in 40 ml of aqueous ethanol, containing 10 mmol of KOH. The mixture was allowed to stand for 10–15 h at room temperature, after which 50–60 ml of water was added, and the colorless precipitate was filtered off, washed with water, and recrystallized from ethanol.

4-Aryl-3-arylacetamido-2*H*,3*H*-1,3-thiazol-2-ones IVa–IVm. *a*. A mixture of 10 mmol of 2*H*,3*H*-1,3,4-oxadiazole-2-thione **Ia**–**Ig** and 10 mmol of α-halo ketone in 20–30 ml of 2-propanol was refluxed for 2–3 h, cooled, and filtered; the colorless precipitate was recrystallized from ethanol.

b. A solution of 10 mmol of 5-substituted 2-aroylmethylthio-1,3,4-oxadiazole **IIa**–**IIh** in 40 ml of ethanol was refluxed for 1 h with 5 ml of concd. HCl, cooled, and filtered; the precipitate was recrystallized.

c. A 10-mmol portion of 4-aryl-3-arylacetamido-2*H*,3*H*-1,3-thiazole-2-thione **VIa**–**VIc** was dissolved in 30 ml of 2 N aqueous NaOH, and 13 ml of 20% aqueous hydrogen peroxide was added with cooling on a water–ice bath. The mixture was allowed to stand at room temperature for 10 h and neutralized with 2 N HCl. The precipitate was filtered off, washed with water, and recrystallized.

4-Aryl-3-arylacetamido-2*H*,3*H*-1,3-thiazole-2-thiones VIa–VIc. A solution of 1.12 g of KOH in 10 ml of water and 20 mmol of CS_2 were added at 0–5°C to a solution of 20 mmol of phenylacetic (**Ia**) or phenoxyacetic (**Ib**) acid hydrazide in 50 ml of methanol. The mixture was stirred for 2 h at 5°C, after which a solution of 20 mmol of α-halo ketone in 25 ml of methanol was added. The resulting mixture was allowed to stand for 10 h at room temperature. Then 5 ml of concentrated HCl was added, the mixture was refluxed for 1 h, and, after cooling, the colorless precipitate was filtered off and recrystallized from ethanol or glacial acetic acid.

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