CHEMISTRY OF SELENOPHENE

LXI. β-Diketones of the Selenophene Series with a 3-Selenienyl Radical*

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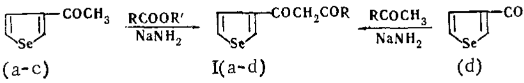
The synthesis of a number of β-diketones and 3, 5-disubstituted pyrazoles with 3-selenienyl radicals has been described.

In one of the preceding communications [1] the synthesis of β-diketones containing α-, β-, or γ-pyridyl radicals, in addition to a 2-selenienyl radical, has been reported. It was shown that these β-diketones are effective inhibitors of the oxidation of silicone liquids used as lubricants and as dispersion media in bodied greases [2].

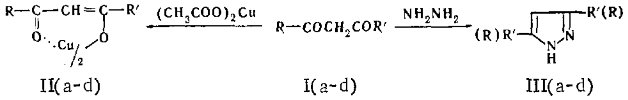
In the present paper we describe the synthesis of β-diketones isomeric with those containing a 3-selenienyl radical—3-(picolinoylacetyl) and 3-(isonicotinoylacetyl)selenophenes and also 3-(2-furoylacetyl)- and 3-(2-thenoylacetyl)selenophenes.

The synthesis of the first three diketones was effected by condensing 3-acetylselenophene with esters of picolinic, isonicotinic, and pyromucic acids, respectively; 3-(2-thenoylacetyl) selenophene was obtained by the reaction of 2-acetylthiophene with methyl 3-selenophenecarboxylate. It was impossible to obtain di(3-selenenoyl)methane by condensing 3-acetylselenophene with methyl 3-selenophenecarboxylate (resinification).



a $R—\alpha\text{-}C_5H_4N$, b $R—\gamma\text{-}C_5H_4N$ } $R'\text{-}C_2H_5$; c $R—\alpha\text{-}C_4H_3O$, d $R—\alpha\text{-}C_4H_3S$ } $R'—CH_3$

On reaction with copper acetate, the β-diketones synthesized readily formed Cu^{2+} complexes, and with hydrazine hydrate they formed 3,5-disubstituted pyrazoles.



$R—\beta\text{-}C_4H_3Se$; $R'—\alpha\text{-}C_5H_4N$ (a),

$\gamma\text{-}C_5H_4N$ (b), $\alpha\text{-}C_4H_3O$ (c), $\alpha\text{-}C_4H_3S$ (d).

Table 1 gives details of the IR and UV spectra (taken in methanol) of the β-diketones with a 3-selenienyl radical that have been synthesized and also the UV spectra (taken in chloroform) of their Cu^{2+} complexes.

From the information given in Table 1, it can be seen that the UV spectra of the β-diketones synthesized, unlike the UV spectra of the isomeric β-diketones with a 2-selenienyl radical [1] have two and not three absorption maxima and these are shifted into the region of shorter wavelengths, as we have found previously for the UV spectra of β-diketones with a 3-selenienyl radical [3]. The intensities of absorption remain high ($\log \varepsilon \simeq 4$).

The UV spectra of the Cu^{2+} complexes of β-diketones with a 3-selenienyl radical have three maxima instead of the two characteristic for the isomeric Cu^{2+} β-diketonates with a 2-selenienyl radical.

The IR spectra of the β-diketones with a 3-selenienyl radical have absorption bands in the 1539–1596 cm^{-1} region (chelate carbonyl) and a broad absorption band in the 2550–2770 cm^{-1} region (chelate hydroxyl), while the absorption bands characteristic for free carbonyl and hydroxy groups are absent; thus, these β-diketones exist in the cis-enolic chelate form [4,5]. The NMR spectra of the β-diketones containing a 3-selenienyl radical synthesized previously [3] and in the present work have been recorded.

To evaluate the enolizing power of the radicals in these β-diketones, which are almost completely enolized, we partially suppressed the enolization by dissolving them in acetone and determined the keto-enol equilibrium from the NMR spectra (Table 2).

The relative concentration of the enolic form was determined by measuring the intensity of the signals from the methylene group of the keto form and from the $=CH—$ group of the enolic form. Since the degree of enolization of the β-diketones depends on the concentration (because of solubility differences), the evaluation of the enolizing power of the radicals was made approximately. It can be seen from the figures of Table 2 that the methyl group has the lowest enolizing capacity and then in rising sequence come the α-furyl, α-thienyl, phenyl, and α-pyridyl groups. We have observed a similar dependence of the degree of enolization on the nature of the radical in the series of β-diketones with 2-selenienyl radicals [6].

The chemical shifts of the signals given in Table 3 were measured with respect to hexamethyldisiloxane as internal standard and were expressed in the units $\delta = \Delta f/60$ millionths of the resonance frequency (ppm). Here Δf is the distance between the signals in Hz and 60 is the working frequency of the INM-3-60 spectrometer.

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*For part LX, see [7].

Table 1

3-(Acylacetyl)selenophenes				Cu^{2+} complexes	
Acyl	λ_{max}, NM	log ε	ν, cm^{-1}	λ_{max}, NM	log ε
Picolinoyl	275, 352	3.83; 4.34	1560, 1580	285, 365, 610*	
Isonicotinoyl	270, 365	4.02; 4.40	1570	300, 355*	
α-Furoyl	277, 363	4.05; 4.51	1578, 1596	305, 365, 640	4.53; 4.78; 1.69
α-Thenoyl	350	4.36	1539, 1595	305, 365, 645*	

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*The intensity of absorption was not determined because of the low solubility of the Cu^{2+} complexes in chloroform.

Table 2

Enolization of 3-(Acylacetyl)-selenophenes in Acetone

Acyl	Molar concentration, %	Content of the enol, %
Acetyl	22	83
Benzoyl	24	95
α-Furoyl	15.5	91
α-Thenoyl	9	90
Picolinoyl	18.5	96

Table 3

Chemical Shifts of the Proton Signals of 3-(Acylacetyl)selenophenes

Acyl	Molar concentration, %	Chemical shift, δ, ppm		
		$-CH_2-$	$=CH-$	$-OH$
Acetyl	22	4.30	6.48	9.4
Benzoyl	24	4.82	7.30	9.55
α-Furoyl	15.5	4.50	6.80	9.12
α-Thenoyl	9	4.80	7.14	9.44
Picolinoyl	18.5	4.89	7.63	9.40

Table 4

3-(Acylacetyl)selenophenes (**Ia-d**)

Acyl	Mp, °C	Empirical formula	Found, %		Calculated, %		Yield, %
			C	H	C	H	
Picolinoyl*	78—79.5	$C_{12}H_9NO_2Se$	51.65 51.73	3.22 3.26	51.81	3.26	76.5
Isonicotinoyl	129.5—130.5	$C_{12}H_9NO_2Se$	51.37 51.37	3.15 3.24	51.81	3.26	76
α-Furoyl**	78—79.5	$C_{11}H_8O_3Se$	49.56 49.26	3.07 3.21	49.45	3.01	94
α-Thenoyl	90—91	$C_{11}H_8O_2SSe$	46.48 46.67	2.93 3.02	46.72	2.84	76

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*Found, %: Se 28.04, 28.13. Calculated, %: 28.38.

**Found, %: Se 29.57, 29.39. Calculated, %: 29.56.

Table 5

Cu^{2+} Complexes of 3-(Acylacetyl)selenophenes (**IIa-d**)

Acyl	Mp, °C	Empirical formula	Found, %		Calculated, %		Yield, %
			C	H	C	H	
Picolinoyl*	272—273.5 decomp.	$C_{24}H_{16}CuN_2O_4Se_2$	47.19 47.29	2.86 2.81	46.65	2.61	86
Isonicotinoyl	285—287 decomp.	$C_{24}H_{16}CuN_2O_4Se_2$	46.16 46.09	2.90 2.83	46.65	2.61	95.5
α-Furoyl**	253—255 decomp.	$C_{22}H_{14}CuO_6Se_2$	44.06 44.32	2.63 2.50	44.34	2.36	94.5
α-Thenoyl	283—284 decomp.	$C_{22}H_{14}CuO_4S_2Se_2$	41.88 41.67	2.46 3.55	42.08	2.24	91

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*Found, %: Se 25.50, 25.63. Calculated, %: 25.56.

**Found, %: Se 26.11, 26.07. Calculated, %: 26.56.

Table 6

(5)3-(3-Selenienyl)-5(3)-R-pyrazoles (**IIIa-d**)

R	Mp, °C	Empirical formula	Found, %		Calculated, %		Yield, %
			C	H	C	H	
α-Pyridyl*	179.5—180.5	$C_{12}H_9N_3Se$	52.48 52.33	3.26 3.20	52.57	3.31	85
γ-Pyridyl	189—190	$C_{12}H_9N_3Se$	52.55 52.55	3.29 3.63	52.57	3.31	81
α-Furyl	186—187.5	$C_{11}H_8N_2OSe$	50.09 49.97	3.22 3.10	50.29	3.05	81.5
α-Thienyl	200—200.5	$C_{11}H_8N_2SSe$	46.40 46.51	2.84 2.93	47.01	2.88	86

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*Found, %: Se 28.56, 28.98. Calculated, %: Se 28.80.

EXPERIMENTAL

3-(Acylacetyl)selenophenes (Ia-d). In drops, 29 mmole of a ketone in 25 ml of absolute ether was added to 63 mmole of sodium amide in 25 ml of absolute ether, the mixture was stirred for 20 minutes. Then 36 mmole of the ester in 20 ml of absolute ether was added and the mixture was heated at 36° C for 3.5 hr, left for 20 hr, poured onto 150 g of ice and 22 ml of acetic acid (in the preparation of compounds Ic and Id the reaction mixture was decomposed with a mixture of 200 g of ice and 50 ml of concentrated hydrochloric acid), and extracted with ether. The ethereal solution was then washed with saturated sodium carbonate solution and dried with magnesium sulfate, the solvent was driven off in vacuum, and the β-diketones were recrystallized from heptane (Table 4).

The Cu^{2+} complexes of the 3-(acylacetyl)selenophenes (IIa-d) were obtained by the reaction of a saturated ethanolic solution of 0.7 mmole of a β-diketone and a saturated aqueous solution of 1 mmole of copper acetate; they were crystallized from acetone (Table 5).

3-(3-Selenienyl)-5-R-pyrazoles (IIIa-d). A mixture of 4.5 mmole of a β-diketone and 1.3 ml of hydrazine hydrate in 10 ml of ethanol was heated in the water bath for 1 hr and the solvent was distilled off in vacuum; the pyrazoles were recrystallized from ethanol (Table 6).

REFERENCES

1. Yu. K. Yur'ev, N. N. Magdesieva, and V. V. Titov, ZhOKh, 32, 3252, 1962.
2. Yu. K. Yur'ev, N. N. Magdesieva, E. M. Oparina, R. I. Kobzova, and N. K. Levkina, Soviet patent no. 160559; Byull. izobr., no. 4, 1964.
3. Yu. K. Yur'ev, N. N. Magdesieva, and A. T. Monakhova, ZhOrKh, 1, 1094, 1965.
4. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, p. 202, 1963.
5. J. V. Love, Jr. and I. N. Ferguson, J. Org. Chem. 30, 3000, 1965.
6. N. N. Magdesieva, V. V. Titov, V. F. Bystrov, V. P. Lezina, and Yu. K. Yur'ev, ZhSKh, 6, 402, 1965.
7. Yu. K. Yur'ev, N. N. Magdesieva, and A. T. Monakhova, KhGS [Chemistry of Heterocyclic Compounds], 4, 645, 1968.

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