

SELENOPHENE CHEMISTRY

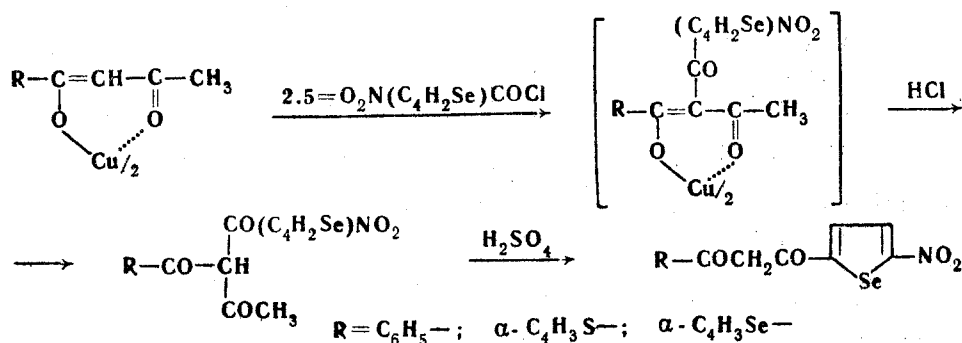
LVII. Selenophene Series β -diketones with a Nitro Group in the Selenophene Ring*

Yu. K. Yur'ev, N. N. Magdesieva, and T. Lesyak

Kimiya Geterotsiklicheskih Soedinenii, Vol. 2, No. 6, pp. 902-904, 1966

Acylation of the copper complexes of benzoyl-, thenoyl-2-, selenoyl-2-acetone with 5-nitroselenophene-2-carbonyl chloride followed by hydrolysis of the resultant triketones is a method of synthesizing β -diketones containing the 5-nitroselenienyl group. ω -Benzoyl-, ω -thenoyl-2-, and ω -selenoyl-2-(5-nitro-2-aceto-selenophene), are prepared in that way, their IR and UV spectra are determined, and the dissociation constants measured. Cu^{2+} complexes are also prepared.

Among β -diketones with various other groups in addition to selenienyl-2 [1-4], those with a nitro group at position 5 in the selenophene are so far unknown. It was possible to synthesize this type of β -diketone by 5-nitroselenophene-2-carbonyl chloride acylation of copper complexes of acylacetones containing a group of an aromatic nature, followed by hydrolysis of the triketone. In this we synthesized ω -benzoyl-, ω -thenoyl-2-, and ω -selenenoyl-2 (5-nitro-2-aceto-selenophenes) in high yield:



The UV spectra (in chloroform) of these β -diketones have three characteristic maxima, and the absorption curves are basically similar to those of other β -diketones, with other groups of an aromatic nature in addition to the selenienyl one. The presence in the β -diketone of the 5-nitroselenienyl group gives rise to an even greater shift of absorption maximum in the longer wavelength region than obtains with selenienyl-2 and -3 groups (Table 1).

Table 1
UV and IR Spectra and Dissociation Constants of β -Diketones Containing Nitroselenienyl Groups

R	$\lambda_{\text{max}}, \text{m}\mu$	$\lg \epsilon$	$\Delta\nu, \text{cm}^{-1}$	pK_{diss}
Phenyl	272-275; 305; 370	4.05; 4.01; 4.34	1324	7.94 ± 0.03
Thienyl-2	260; 307-310; 405	3.83; 3.98; 4.44	1323; 1354	7.62 ± 0.05
Selenienyl-2	265; 310; 410	3.85; 3.98; 4.38	1320; 1342	7.65 ± 0.02

The IR spectra show absorption bands characteristic of aromatic nitro compounds (Table 1), while bands characteristic of free carbonyl and hydroxyl groups (at $1700\text{--}1720 \text{ cm}^{-1}$ and $3500\text{--}3600 \text{ cm}^{-1}$, respectively) are absent, indicating that these β -diketones exist in the enol form.

* For Part LVI see [7].

Determination of the dissociation constant by potentiometric titration [5] in water-dioxane solution (solubility of the reagents in water being negligible) showed (Table 1) that introduction of the nitroselenienyl group into β -diketone molecules increases the degree of dissociation.

When treated with copper acetate the β -diketones gave Cu^{2+} intramolecular complexes.

Table 2
Triketones and β -Diketones Containing the 5-Nitroselenienyl Group and the Cu^{2+}
Complexes of the β -Diketones

R	Mp, °C	Formula	Found, %		Calculated, %		Yield, %
			C	H	C	H	
Acetylaryl (5-nitroselenoyl-2) methanes							
Benzoyl	124—125	C ₁₅ H ₁₁ O ₅ NSe	49.61; 49.63	3.11; 3.09	49.46	3.04	88
Thenoyl-2	158—159	C ₁₃ H ₉ O ₅ NSe	42.13; 41.93	2.64; 2.57	42.06	2.45	90
Selenenoyl-2	160—161	C ₁₃ H ₉ O ₅ NSe ₂	37.65; 37.55	1.98; 1.76	37.43	2.17	85
ω-Aroyl (5-nitro-2-acetoselenophenes)							
Benzoyl	147—148	C ₁₃ H ₉ O ₄ NSe	48.67; 48.60	3.43; 3.53	48.46	2.82	94
Thenoyl-2	146—147	C ₁₁ H ₇ O ₄ NSSe	40.05; 40.35	2.25; 1.99	40.25	2.15	92
Selenoyl-2	145—146	C ₁₁ H ₇ O ₄ NSe ₂	35.27; 35.09	2.38; 2.35	35.22	1.88	93
Cu ²⁺ complexes of ω-aroyl (5-nitro 2-acetoselenophenes)							
Benzoyl	326 (decomp.)	C ₂₆ H ₁₆ O ₈ N ₂ Se ₂ Cu	44.01; 43.92	1.93; 1.87	44.24	2.28	95
Thenoyl-2	307 (decomp.)	C ₂₂ H ₁₂ O ₈ N ₂ S ₂ Se ₂ Cu	36.61; 36.43	2.15; 2.05	36.80	1.80	96
Selenenoyl-2	311 (decomp.)	C ₂₂ H ₁₂ O ₈ N ₂ Se ₄ Cu	32.21; 32.34	1.22; 1.10	32.55	1.49	93

Table 2 gives physical properties and yields of triketones, β -diketones containing the 5-nitroselenienyl-2 group, and their copper complexes.

Experimental

Acetylaryl (5-nitroselenoyl-2) methanes (I). 0.02 mole of the Cu complex of the aroyl (benzoyl-, thenoyl-2, or selenoyl-2) acetone and 0.02 mole 5-nitroselenophene-2-carbonyl chloride (mp 54° C [6]) in 100 ml dry CHCl_3 was stirred for 15 hr at 0° and then for 5 hr at 20° C, the products solution washed with 80 ml dilute HCl (1:1), the CHCl_3 layer separated off, dried over MgSO_4 , the CHCl_3 vacuum-distilled off, and the residue recrystallized from MeOH-benzene (3:1).

ω -Aroyl (5-nitro-2-acetoselenophenes) (II). 1.5 ml concentrated H_2SO_4 in 10 ml EtOH was added slowly to 0.01 mole triketone I, the mixture heated on a water-bath for 30 min, the precipitate separated off, washed twice with EtOH, and recrystallized from MeOH-benzene (3:1).

Complex of II with Cu^{2+} . Prepared by treating a saturated EtOH solution of II with aqueous Cu acetate solution; the precipitate was washed with EtOH and water. Yields, physical properties, and analyses of the triketones and β -diketones thus prepared and containing the 5-nitroselenienyl group, and of their Cu^{2+} complexes, are given in Table 2.

REFERENCES

1. Yu. K. Yur'ev and N. N. Mezentsova, *ZhOKh*, **31**, 1449, 1961.
2. Yu. K. Yur'ev, N. N. Magdesieva, and V. V. Titov, *ZhOKh*, **32**, 3252, 1962.
3. Yu. K. Yurev, N. N. Magdesieva, and V. P. Brysova, *ZhOKh*, **33**, 2578, 1963.
4. Yu. K. Yur'ev, N. N. Magdesieva, and V. V. Titov, *ZhOKh*, **33**, 2577, 1963.
5. A. Albert and E. Serjeant, *Ionization Constants of Acids and Bases* [in Russian], Khimiya, Moscow-Leningrad, 1964.
6. Yu. K. Yur'ev and E. L. Zaitseva, *ZhOKh*, **29**, 3644, 1959.
7. Yu. K. Yur'ev, M. A. Gal'bershtam, and I. I. Kandror, *KhGS* [Chemistry of Heterocyclic Compounds], 897, 1966.