LETTERS TO THE EDITOR

SELENOPYRYLIUM SALTS FROM 1,5-DIKETONES

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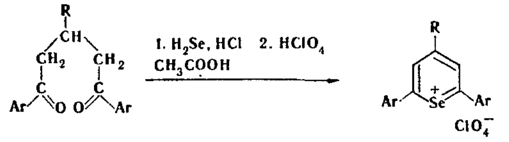
Selenopyrylium salts IIa-e (see Table 1) were obtained by treatment of 1,5-diaryl-substituted 1,5-diketones Ia-e with a mixture of hydrogen selenide and hydrogen chloride. The reaction probably proceeds in a manner similar to that used to produce thiopyrylium salts [1].



Ia-e IIa-e

Hydrogen selenide was passed for 1 h through a solution of 5 g (0.018 mole) of 1,3-dibenzoylpropane in 80 ml of glacial acetic acid at 15°, after which hydrogen selenide and hydrogen chloride were passed simultaneously through the mixture at 25° for 3 h. The yellow precipitate of 2,6-diphenylselenopyrylium chloride was obtained by addition of 200 ml of dry ether and converted to the perchlorate with 20% perchloric acid. Salts IIb-e were similarly obtained. The results of the experiments are presented in Table 1 (IIa was crystallized from nitromethane, while IIb-e were crystallized from glacial acetic acid).

The selenopyrylium salts were more deeply colored than their sulfur analogs, while IIa had a considerably higher color than the diphenylpentamethylidynecarbonium salt (λ_{max} of which is 570 nm) [2]; this is in agreement with the theory in [3]. The introduction of electron-donor OCH_3 and CH_3 groups into the p,p' positions of the 2,6-phenyl substituents leads to deepening of the color. On the other hand, electron-donor CH_3 and C_6H_5 groups in the 4 position of these salts causes a hypsochromic shift of the absorption maximum. The latter is in agreement with the Dewar–Knott rule [4, 5], if IIa-e are considered to be

TABLE 1. Selenopyrylium Perchlorates (IIa-e)

Compound	R	Ar	Decomp. point, °C	Empirical formula	Found, %		Calc., %		λ_{max}, nm (lg ε)*	Yield, %
					Se	Cl	Se	Cl		
IIa	H	C_6H_5	187	$C_{17}H_{13}ClO_4Se$	19,8		20,0		420 (4,33)	19
IIb	CH_3	C_6H_5	196	$C_{18}H_{15}ClO_4Se$	19,2	8,6	19.3	8,7	410 (4,33) (390)†	17
IIc	CH_3	$C_6H_4CH_3$-p	240	$C_{20}H_{19}ClO_4Se$	18,1	8,2	18.0	8,1	434 (4,47) (420)	13
IId	CH_3	$C_6H_4OCH_3$-p	218	$C_{20}H_{19}ClO_6Se$	16.4	7,3	16,8	7,6	482 (4,48) (465)	14
IIe	C_6H_5	C_6H_5	205	$C_{23}H_{17}ClO_4Se$	16,7		16,8		390 (4,44) (368)	30

*The spectra were recorded from acetonitrile solutions containing 1% perchloric acid (sp. gr. 1.67).

†The λ_{max} values for the analogous thiopyrylium salts that we synthesized are presented in parentheses.

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closed (by the heteroatom in the ring) diphenylpentamethylidynecarbonium cations. The IR spectrum of 2,4,6-triphenylselenopyrylium perchlorate is very similar to the IR spectrum of 2,4,6-triphenylthiopyrylium perchlorate. The spectra of both compounds are characterized by three intense bands, the middle one of which for IIe is shifted somewhat to lower frequencies (in CCl_4, 1426, 1459, and 1562 cm^{-1} for IIe, and 1426, 1470, and 1566 cm^{-1} for its sulfur analog). The bands at 1426 cm^{-1} is also retained for 2,6-diphenylselenopyrylium salts IIa, b, while the intensities of the two other bands are markedly weakened, particularly in the case of IIa.

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