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DISELENIENYLDENECYCLOALKANONES

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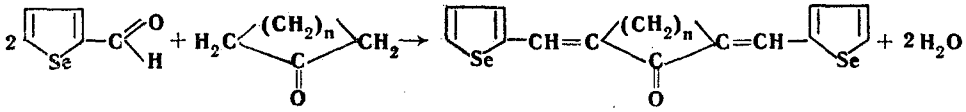
Crotonoid condensation of 2 moles of 2-selenophenaldehyde and 1 mole of acetone, cyclopentanone, cyclohexanone, or cyclheptanone, gave diselenienylidenacetone and the corresponding diselenienylidinecycloalkanones. The electronic absorption spectra in ethanol and in sulfuric acid-glacial acetic acid were measured, and are discussed, similarly with the IR spectra of the solids over the range 1800–600 cm^{-1}. All the compounds investigated showed halochromism.

Two of us [1] have previously published the results of research on the electronic absorption spectra and halochromic properties of dibenzylidenecycloalkalonones, and their furan and thiophene analogs. It was of interest to investigate the properties of hitherto undescribed 5, 6, and 7-membered ring diselenienylidenecycloalkanones, and to compare them with the similar properties of diselenienylidenacetone, previously prepared [2] by condensing selenienylidene-2-acetone with 2-selenophenaldehyde.

The requisite unsaturated ketones were synthesized by crotonoid condensation of acetone, cyclopentanone, cyclohexanone, and cycloheptanone, with 2-selenophenaldehyde in aqueous ethanol solution, in the presence of sodium hydroxide solution, as previously described by us [3]:



n = 0 (I), 2 (II), 3 (III), and 4 (IV, V) (see Table 1).

Preparation of diselenienylideneacetone by direct condensation of selenophenaldehyde with acetone has the advantage that synthesis is effected in one stage, the yield being considerably greater, and the melting point of the product higher (139° C), than previously [2] (128°).

The reaction of 2-selenophenaldehyde with cyclopheptanone gives two compounds, both of which, according to their elementary analyses, correspond to a product of crotonoid condensation between 2 moles of aldehyde, and 1 mole of ketone. In the presence of small quantities of alkali, the main product is IV, mp 195° C, while considerable amounts of catalyst lead to formation of a mixture of IV and V, which can be separated into its individual components by crystallization (V has mp 159° C). It can be postulated that these compounds are either geometric or conformational isomers; however, study of their UV and IR spectra did not unequivocally settle the question.

Electronic absorption spectra in ethanol, and in 30% sulfuric acid in glacial acetic acid, and IR spectra of tablets with KBr in the region 1800–600 cm^{-1} (see Table 2 and Fig. 1), were measured for all the compounds. The compounds studied had characteristic absorption curves which can be used to identify them.

When ketones IV are dissolved in sulfuric acid-glacial acetic mixtures of various compositions, an isobestic point is found, (Fig. 2), confirming the occurrence of acid-base equilibrium, and formation of the corresponding conjugated carbonium ions. The longwave absorption for acid solutions is displaced bathochromically by 155–170 mμ in comparison with λ_{max} for an ethanol solution, so that all the ketones have well-defined halochromic properties.

Inclusion of the carbonyl group in a 5-membered alicyclic ring considerably improves conjugation conditions in the molecule, and this shows up by the absorption maximum II being shifted 19–23 mμ as compared with I. This is due to the carbonyl group in the cyclopentane ring being a better conductor of conjugation than when it is in an open chain, because of orbital rehybridization, and coplanarity in the former case [1].

The cyclohexane (III) ring exhibits less bathochromic action; in ethanol it is 4 mμ, in acid 18 mμ.

As compared with I, the cycloheptanone derivatives IV and V absorb in the shorter wave region. In neutral solution the hypsochromic effect is 12–32 mμ, and for IV in acid solution it is 20 mμ. Here, obviously, conditions for conjugation are worsened, because a Pitzer strain starts to appear in the compounds, and they assume (spatial) configurations such that coplanarity of the carbonyl group with the exocyclic double bonds is destroyed.

Comparison of the electronic absorption spectra of compounds I–V with the spectra of the analogous dibenzylidenecycloalkanones and their furan and thiophene analogs [1] shows that replacement of the aromatic rings by selenophene ones results in sharp deepening both of the natural color (by 57–76 mμ) and the halochromic color (by 73–108 mμ); similar replacement of furyl and thienyl by selenienyl also leads to a bathochromic shift, though a considerably smaller one (by 3–17 mμ). This confirms the previously noted [4] decrease in bathochromic and static electronic effect in the order 2-selenienyl > 2-thienyl > 2-furyl > phenyl.

It is characteristic that when the carbonyl group is included in a 5-membered ring, the frequency of the carbonyl group's valence vibrations increase by 15 cm^{-1} (Table 2), due to change in the character of the sp-hybridization of the valence σ orbitals of carbon, which is in agreement with what is stated in the literature [5]. The vibration for the carbonyl group in unstrained 6- and 7-membered rings (III–V) are already diminished by 5–10 cm^{-1} compared with I, with a carbonyl group in an open chain. It can also be noted that there is considerable lowering of $\nu_{C=O}$ for the α, β-unsaturated ketones investigated, compared with $\nu_{C=O}$ for ordinary aliphatic ketones without a double bond.

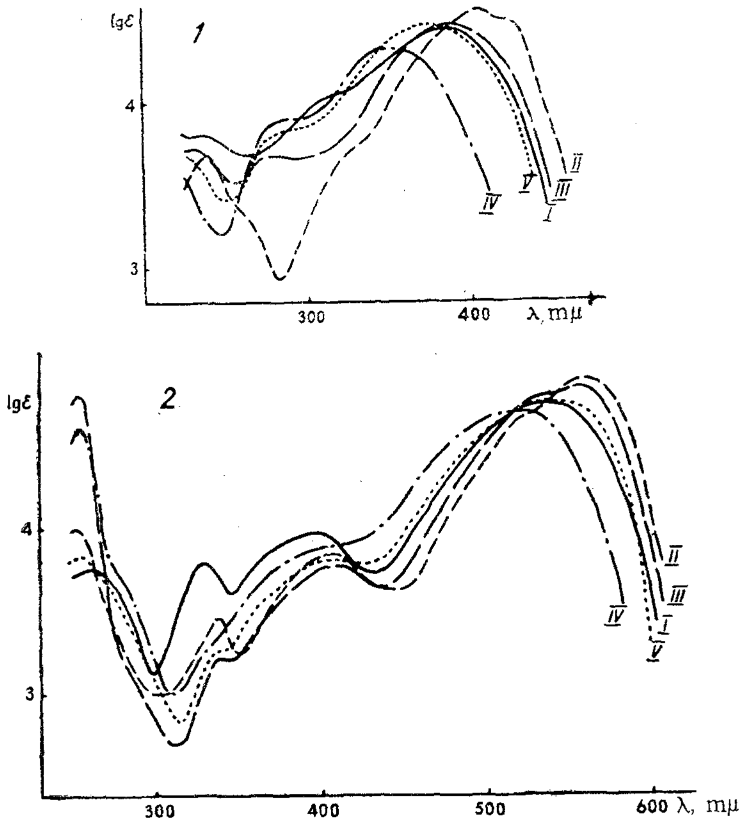


Fig. 1. Absorption curves: 1) in ethanol; 2) in a 30% solution of sulfuric acid in glacial acetic acid.

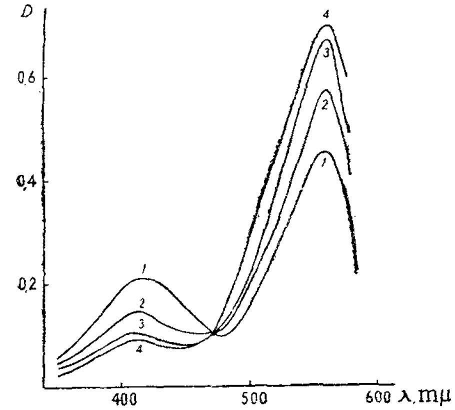


Fig. 2. Absorption curves of diselenienylidenecyclopentanone (II) in sulfuric acid plus glacial acetic acid. H_2SO_4 concentration: 1) 1%; 2) 5%; 3) 7%; 4) 9%.

In ketones II–IV double bond and carbonyl group have a fixed s-cis configuration. As postulated [6], this configuration is manifest in IR spectra by $\nu_{C=C}$ having a greater intensity than $\nu_{C=O}$. In point of fact even qualitative comparison of intensities of appropriate bands confirms this deduction (Table 2). It is of interest that in diselenienylideneacetone (I), $\nu_{C=C}$ intensity is higher than that of $\nu_{C=O}$ one, and obviously it also occurs in the corresponding s-cis conformations.

We shall later make a detailed study of the characteristic vibrations of the selenophene ring in α, β-unsaturated ketones. However, it is already possible to state that the selenophene ring can be detected by ring vibration frequencies at 1555–1595 cm^{-1} and 1427–1438 cm^{-1}, and obviously by – C – Se – valence vibrations at 695–715 cm^{-1} [7].

Experimental

Ketones I-III were synthesized by a previously described method [3].

Table 1

Diselenienylidenacetone and the Corresponding Cycloalkanones

Compound Number	Compound Name	Mp, °C (solvent)	Appearance	Formula	Se, %		Yeild, %
					Found	Calculated	
I	1,5-Diselenienylpentadien-3 one	139 (CH_3OH)	Yellow plates	$C_{13}H_{10}OSe_2$	46.51; 46.55	46.43	80
II	2,5-Diselienylidenecyclopentanone	227 (C_6H_6)	Yellow needles	$C_{15}H_{12}OSe_2$	43.26; 43.14	43.12	51
III	2,6-Diselenienylidenecyclhexanone	152 (CH_3OH+ $+C_6H_6$)	Yellow needles	$C_{16}H_{14}OSe_2$	41.48; 41.50	41.54	44
IV	2,7-Diselenienylidenecycloheptanone	195 (C_6H_6)	Pale-yellow plates	$C_{17}H_{16}OSe_2$	40.00; 39.98	40.06	35
V	2,7-Diselenienylidenecycloheptanone	159 (CH_3OH+ $+C_6H_6$)	Yellow needles	$C_{17}H_{16}OSe_2$	39.84; 40.26	40.06	3.5

2,7-Diselenienylidenecycloheptanones (IV,V). 0.02 mole 2-selenophenealdehyde and 0.01 mole cycloheptanone were dissolved in 10 ml MeOH, and 1 ml 10% aqueous NaOH added. After 24 hr the crystals of IV were filtered off, mp 195° C (ex benzene).

Table 2

Spectrum Properties of Diselenienylidenacetone and-cycloalkanones

Compound Number	Electronic spectra λ_{max}, $m\mu/\varepsilon_{max}$		IR spectra ν, cm^{-1} (% transmission)			
	In EtOH	In 30% H_2SO_4 solution in glacial AcOH	C=O	C=C	Selenophene ring	—C—Se—
I	386/28900 inflection 315, 245/8100	542/56300, 400/9550 330/6300, 262/6000	1670 (46)	1610 (77)	1575 1438 (50) (58)	715 (58)
II	inflection 420, 405/36800 inflection 325, 238/5000	565/78000 410/7300, 340/2900	1685 (64)	1600 (84)	1595 1427 (84) (65)	695 (67)
III	390/30200 280/5000, 232/5500	560/78000 415/6200, 340/2900	1660 (50)	1593 (85)	1555 1430 (65) (58)	696 (66)
IV	inflection 354/22000 290	522/50000 400/7600, 355/3800	1665 (49)	1612 (60)	1593 1438 (60) (49)	713 (62)
V	inflection 374/29500 285	545/55000. 410/6800 inflection 340, 255/7000	1660 (48)	1591 (72)	1556 1430 (60) (55)	700 (58)

When the experiment was repeated, but using 5 ml of the NaOH solution, the product was an oil, from which V crystallized out in the cold, mp 159° C (ex MeOH-benzene). Heating the oil remaining in the filtrate gave crystals of IV.

2,4-Dinitrophenylhydrazone of diselenienylidenacetone, mp 189° C, λ_{max} in $CHCl_3$ 440 mμ. Found: Se 30.42, 30.10%. Calculated for $C_{19}H_{14}N_4O_4Se_2$: Se 30.35%.

Spectrophotometric study. A SF-4 instrument was used to measure the UV and visible absorption spectra in ethanol and 30% H_2SO_4 in glacial AcOH, the concentrations of the compounds being $2-3 \times 10^{-5}$ mole/l. For each solution in acid the stability of the compound with time was investigated as described in [8]. The spectra were measured while they were practically constant. The solvents were purified for optical purposes as described in [9].

The IR spectra of the ketones studied were measured with a UR-10 spectrophotometer, the compounds being tabletted with KBr, using 2 mg compound per 100 mg KBr.

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