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PHOTOCHEMICAL OXIDATION OF 4H-SELENO(THIO)PYRANS

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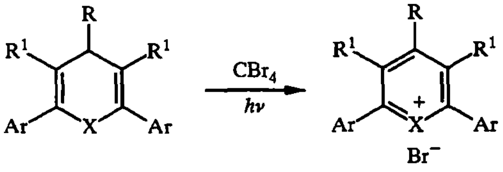
Oxidation of solutions of 4H-thiopyrans and 4H-selenopyrans to the corresponding heteroaromatic cation bromide occurs on irradiation with ultraviolet light in the presence of CBr_4. Reaction takes place by a free radical chain mechanism. The presence of $CHBr_3$ and C_2Br_6 in the reaction mixture was detected chromatographically.

2,4,6-Triphenyl-4H-pyran is capable of photochemical oxidation in a medium of carbon tetrachloride. Assuming initial homolytic fission of carbon tetrachloride with subsequent reaction of the resulting particles by a free radical chain mechanism, including a one-electron transfer step, the authors of [1] used benzoyl peroxide as reaction initiator and the reaction was clearly accelerated in UV light. It is effective to use CBr_4 for similar reactions in photomaterials [2]. It should be noted that 4H-thiopyrans and 4H-selenopyrans have not hitherto been subjected to photochemical oxidation.

Under conditions of photochemical oxidation 4H-seleno(thio)pyrans I-IV are capable of conversion into the corresponding heteroaromatic cations (the results of the experiments carried out are given in Table 1). The reactions were carried out in carbon tetrachloride or chloroform with initiation of the carbon tetrabromide in the reaction medium by UV light. In this reaction system homolytic bond fission of CBr_4 and not of CCl_4 occurs, which is confirmed by literature data [2].



I–IV

V–VIII

I, V X = Se, Ar = R = Ph, R^1 = H; II, VI X = Se, Ar = Ph, R = R^1 = H;III, VII X = S, Ar = Ph, R = $C_6H_4OCH_3$-*p*, R^1 = H; IV, VIII X = Se, Ar = $C_6H_4OCH_3$-*p*, R^1 = CH_3, R = H

The time for complete conversion of chalcogenopyrans I-IV into the corresponding heteroaromatic cations was from 10 min to 2 h. The ratio of chalcogenopyran to CBr_4 (from 1:1 to 1:1.4) proved to have no significant effect on the yield of final product.

2,4,6-Triphenylselenopyrylium (V), 2,6-diphenylselenopyrylium (VI), 4-(*p*-methoxyphenyl)-2,6-diphenylthiopyrylium (VII), and 2,6-di(*p*-methoxyphenyl)-3,5-dimethylselenopyrylium (VIII) bromides were obtained by this reaction. In addition to these chalcogenopyrylium salts, hexabromoethane and bromoform were detected in the reaction mixtures by GLC, which confirms the free radical mechanism of the conversion.

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Under the reaction conditions in the presence of oxygen of the air, selenopyran IV forms salt VIII in low yield (28%), increasing sharply (to 72%) on carrying out the oxidation in an inert atmosphere. The conversion of IV to VIII may also take place in ordinary light with short term initiation by UV light. This may be explained by the effect of sensitization of the resulting selenopyrylium salt VIII, alone of salts V-VIII, which has intense absorption in the visible region of the spectrum. A similar phenomenon was described in [2]. In our case it is suggested that salt VIII absorbs light quanta in the visible region of the spectrum, passes into an excited state, and relays the energy to a complex of chalcogenopyran (HP) with CBr_4, which decomposes to chalcogenopyrylium bromide VIII and bromoform.

$$\begin{array}{rcl} \mathrm{VIII} & \xrightarrow{h\nu} & \mathrm{VIII}^{\bullet} \\ \mathrm{VIII}^{\bullet} + \mathrm{CBr_4{\cdot}HP} & \longrightarrow & \mathrm{VIII} + \mathrm{CBr_4{\cdot}HP}^{\bullet} \\ \mathrm{CBr_4{\cdot}HP}^{\bullet} & \longrightarrow & \mathrm{VIII} + \mathrm{CHBr_3} \end{array}$$

The structure of the obtained salts V-VIII was confirmed by the results of elemental analysis and data of ^{1}H NMR spectra (Tables 1,2).

TABLE 1. Conditions for Photochemical Oxidation of 4H-Chalcogenopyrans I-IV and Characteristics of the Obtained Chalcogenopyrylium Salts V-VIII

Reaction conditions			Reaction product	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
chalcogenopyran, mmol	CBr_4, mmol	solvent (15 ml)			C	H	N		
1.0	1.0	CCl_4	V	$C_{23}H_{17}BrSe$	60.72 61.08	3.55 3.79	—	130-134	69
1.0	1.0	CCl_4	VI	$C_{17}H_{13}BrSe$	53.90 54.28	3.11 3.48	—	119-120	72
1.4	2.0	$CHCl_3$	VII	$C_{24}H_{19}BrOS$	66.90 66.21	4.35 4.40	7.44 7.37	148-150	70
1.3	1.3	CCl_4	VIII	$C_{21}H_{21}BrO_2Se$	54.69 54.33	4.45 4.56	—	130-132	28

TABLE 2. Data of ^{1}H NMR Spectra of the Synthesized Compounds

Chalcogenopyrylium salt	Solvent	Chemical shifts, δ, ppm, coupling constants (*J*), Hz
V	$CF_3COOD:(CD_3)_2SO$, 1:1	8.51 (2H, s, $H_{R'}$); 7.31-7.75 (15H, m, Ph)
	$CDCl_3$	7.15-7.81 (17H, m, Ph + $H_{R'}$)
VI	$CF_3COOD:(CD_3)_2SO$, 1:1	8.58-8.82 (3H, m, H_R + $H_{R'}$); 7.84-7.96 (4H, m, Ph) 7.60-7.72 (6H, m, Ph)
VII	$CDCl_3$	8.83 (2H, s, $H_{R'}$); 8.29-8.63 (6H, m, C_6H_5 + C_6H_4) 7.51-7.69 (6H, m, C_6H_5 + C_6H_4) 7.00 (2H, d, J = 8.9, C_6H_4); 3.75 (3H, s, OCH_3)
VIII	CD_3OD	8.77 (1H, s, H_R); 7.76 (4H, d, J = 8.6, C_6H_4) 7.08 (4H, d, J = 8.6, C_6H_4); 3.88 (6H, s, OCH_3) 2.56 (6H, s, CH_3)

EXPERIMENTAL

The progress of reactions and the purity of the compounds obtained was checked by TLC on Silufol UV 254 plates in the systems hexane–ether–chloroform (3:1:1) and hexane–ether (6:1, 10:1, 25:1), visualizing with iodine vapor. The ^{1}H NMR spectra were obtained on a Varian FT 80A spectrometer at 30°C. Operating frequency was 80 MHz, internal standard was HMDS (0.15 ppm relative to TMS). The GLC analysis was carried out on a LKhM-8MD instrument with a flame-ionization detector. The liquid phase was DC-550 silicone oil and the carrier Chromaton N-AW-HMDS 0.2-0.25. Column size was 1500 × 4 mm. The UV source was a DRT-125 lamp (250-400 nm).

2,4,6-Triphenyl-4H-selenopyran (I) and 2,6-Diphenyl-4H-selenopyran (II) were obtained by the known procedure of [3]. 4-(*p*-Methoxyphenyl)-2,6-diphenyl-4H-thiopyran (III) was synthesized as described in [4], 2,6-di(*p*-methoxyphenyl)-3,5-dimethyl-4H-selenopyran (IV) was obtained in 82% yield as described in [5], and the initial selenopyrylium salt was obtained by the known procedure of [6].

Photochemical Oxidation of 4H-Chalcogenopyrans I-IV (General Method). A solution of seleno(thio)pyran and carbon tetrabromide in chloroform or carbon tetrachloride (the reactant ratios are given in Table 1) was stirred in a reactor, with a built-in source of UV irradiation fitted with a quartz jacket with water cooling, until complete disappearance of the starting material according to TLC. The reaction mixture was diluted with absolute ether, the precipitated crystals of salts V-VIII were filtered off, washed with ether, dried, and reprecipitated from chloroform or acetonitrile with ether.

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