3,5-DI-tert-BUTYL-o-BENZOQUINONE AS A REAGENT FOR OXIDATIVE DEHYDROGENATION OF 9R-sym-NONAHYDRO-10-CHALCOGENOANTHRACENES

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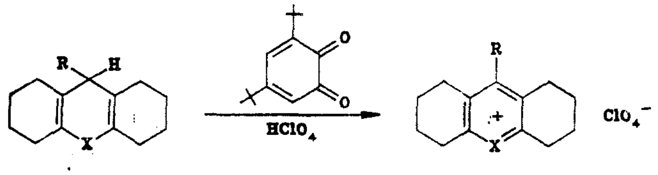
3,5-Di-tert-butyl-o-benzoquininone is a convenient reagent for the oxidative dehydrogenation of 9R-sym-nonahydro-10-chalcogenoanthracenes. The good solubility of o-quinone itself and the corresponding pyrocatechol facilitates the isolation of the salts of 10-chalcogenoanthrenes, which do not require additional purification. Unlike trityl perchlorate, o-quinone has mild oxidizing characteristics and does not give rise to elimination of the substituents. The synthesis of three new chalcogenopyrans and nine chalcogenopyrylium salts is described.

The oxidative dehydroaromatization of chalcogenopyrans is one of the principal methods for the synthesis of chalcogenopyrylium salts [1-4]. As found, o-quinones, which possess high oxidation potentials and dehydrogenating activity, are unexpectedly absent from the wide range of oxidizing agents [5]. The reason for this is probably experimental difficulties due to the instability of the majority of the o-quinones. p-Quinones also have not found wide use for the synthesis of pyrylium salts on account of the low solubility of the respective hydroquinones, which makes isolation of the required compounds difficult. Since this shortcoming is absent in 3,5-di-tert-butyl-o-quinone (I), in the present work we investigated the possibility of dehydrogenating a series of 9R-sym-nonahydro-10-chalcogenoanthracenes (II-X) by the quinone (I).

It was established that compounds (II-X) undergo dehydroaromatization by o-quinone (I) very readily in the presence of perchloric acid in polar and nonpolar solvents (acetonitrile, acetone, ether). The processes take place most quickly in polar solvents, but the best preparative yields of the respective salts are obtained with ether as solvent. In this case, the crystalline reaction products (XI-XIX) separate from the reaction mixture in the individual state and in most cases do not require additional purification. The formation of side products resulting from the elimination of the substituent at position 9, which is typical of trityl perchlorate, is not observed, and the yields of the pyrylium salts are close to quantitative.



II-X XI-XIX

II—IV, XI—XIII R=H; V—VII, XIV—XVI R=C_6H_5; VIII—X, XVII—XIX R==$C_6H_4OCH_3$-*p*; II, V, VIII, XI, XVII X=O; III, VI, IX, XII, XV, XVIII X=S; IV, VII, X, XIII, XVI, XIX X=Se

The oxidation rate of the chalcogenopyrans is strongly affected by the nature of the heteroaromatic compound and by the nature of the substituent at the tetragonal carbon atom of the heterocycle. The observed decrease in rate in the order thiopyran » selenopyran ≳ pyran corresponds to the stability of the respective cations: thiopyrylium > selenopyrylium ≈ pyrylium [6, 7].

The negative effect of the aryl substituents on the process rate is due, in our opinion, not only to the decrease in the number of mobile hydrogen atoms, but also to the appearance of steric hindrances during the formation of the intermediate re-

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TABLE 1. Conditions and Results of the Oxidation of Compounds (II-IX) by o-Quinone (I) in the Presence of Perchloric Acid (chalcogenopyran–quinone–ratios 1:1.5:2)

Initial chalcogenopyran	Reaction time	Reaction product	Mp, °C	Yield, %
II	5 min	XI	170 ... 171 [16]	81
III	3 min	XII	120 ... 122 [16]	80
IV	5 min	XIII	126 ... 127 [12]	21*
V	6 h	XIV	208 ... 209	96
VI	40 min	XV	173 ... 175	98
VII	3,5h	XVI	158 ... 159	91
VIII	5 h	XVII	171 ... 172	80
IX	1 h	XVIII	126 ... 127	95
X	4,5 h	XIX	167 ... 168	89

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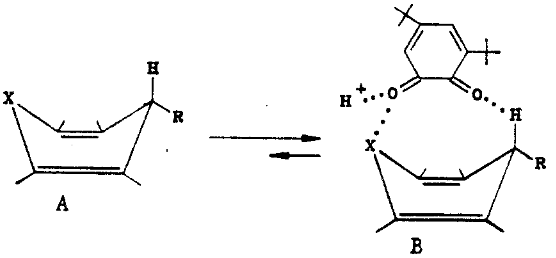
*With the product from the reduction of the quinone (I) the perchlorate (XIII) forms an adduct which is difficult to isolate and separate.

action complex. It is known [8, 9] that the chalcogenopyran ring has the form of a flattened boat and undergoes inversion about the X–$C_{(\gamma)}$ axis in solution. The introduction of a bulky substituent at the γ position of 3,5-substituted chalcogenopyrans gives rise to a displacement of the equilibrium toward conformer A with the pseudoaxial arrangement of the substituent, which is unsuitable for the formation of the intermolecular intermediate complex:



In addition, it is necessary to allow for the possibility of stabilization of the radical-cation intermediates, which presumably arise during oxidation of the chalcogenopyrans by the quinone according to the SET mechanism, by the aryl substituents.

The structures of the synthesized perchlorates (XI-XIX) were confirmed by the elemental analysis and by the IR spectra, which contain characteristic absorption bands for the chalcogenopyrylium salts in the region of 1525-1610 cm^{-1}.

EXPERIMENTAL

The IR spectra were recorded in tablets with potassium bromide on a Specord IR-75 spectrometer. The processes were monitored by TLC on Silufol UV-254 plates with a 100:1 mixture of hexane and ether as eluant and iodine vapor as developer.

The initial chalcogenopyrans (II-VI) were obtained by known methods [10-13], and compounds (VII-X) were synthesized for the first time.

9-Phenyl-sym-nonahydro-10-selenaanthracene (VII). We mixed 14.2 g (0.05 mole) of 13-oxo-8-phenyltricyclo[7.3.1.$0^{2,7}$]tridecan-2-one with 0.2 g of sodium hydroxide and heated the mixture at 200°C for 5 min. The hot solution was dissolved in 50 ml of acetic acid, nitrogen was passed into the solution for 30 min, and hydrogen selenide was then passed for 30 min. A 1.5-ml portion of concentrated hydrochloric acid was added, and the mixture was stirred for 3 h while the passage of hydrogen selenide was continued. The precipitate was filtered off and boiled for 30 min in 30 ml of acetone and cooled, and 13.16 g of (VII) was isolated in the form of crystals; mp 95-96°C. IR spectrum, cm^{-1}: 1640, 1695 (C=C). The yield was 81%.

The selenide (X) was obtained similarly from 13-oxo-8-(p-methoxyphenyl)tricyclo[7.3.1.$0^{2,7}$]tridecan-2-one; mp 82-83°C (from acetone). IR spectrum, cm^{-1}: 1618, 1695 (C=C). The yield was 65%.

9-(4-Methoxyphenyl)-sym-nonahydro-10-oxaanthracene (VIII). A suspension of 94.2 g (0.3 mole) of 13-oxo-8-(p-methoxyphenyl)tricyclo[7.3.1.$0^{2,7}$]tridecan-2-one was boiled for 10 h in 200 ml of a 1:1 mixture of acetic anhydride and acetic acid. The mixture was cooled, and 63.2 g of (VIII) was filtered off in the form of crystals; mp 86-87°C (from acetone). IR spectrum, cm^{-1}: 1670, 1705 (C=C). The yield was 72%.

9-(4-Methoxyphenyl)-sym-nonahydro-10-thiaanthracene (IX). A suspension of 59.2 g (0.2 mole) of (VIII) in 200 ml of acetic acid was saturated with hydrogen sulfide for 30 min, 3 ml of concentrated hydrochloric acid was added, and the mixture was stirred for 4 h while the bubbling of hydrogen sulfide was continued. The reaction mixture was left for 12 h, the precipitate was separated, 120 ml of acetone was added to it, and the mixture was boiled for 1 h. The product was cooled, and 42.5 g of (IX) was filtered off in the form of crystals; mp 66-67°C (from acetone). IR spectrum, cm^{-1}: 1660, 1695 (C=O). The yield was 68.1%.

The elemental analyses of compounds (VII-X) agreed with the calculated data.

Oxidation of Compounds (II-X) by the Quinone (I). A mixture of 0.01 mole of (II-X), 0.015 mole of the quinone (I), and 0.02 mole of 70% perchloric acid was stirred in 100 ml of ether until the reaction was complete (monitored by TLC). The crystalline perchlorates (XI, XII, XIV-XIX) were filtered off (Table 1).

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