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REACTIVITY OF CYCLIC SULFIDES IN REACTIONS WITH QUINONES

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Sulfonium salts are obtained by the reaction of cyclic sulfides with 1,4-benzoquinone and 5,8-quinolinedione in an acidic medium. It is shown by the method of concurrent reactions that the introduction of alkyl substituents into molecules of thiacyclopentane and thiacyclohexane decreases the reactivity of the sulfides. Quinolinedione is less reactive towards sulfides than is benzoquinone.

It is known [1, 2] that sulfides in an acidic medium react with quinolines, forming sulfonium salts. There is no information in the literature concerning the special behavior in this reaction of quinones that contain a heterocyclic ring, expecially quinolinediones. Nor is there any on the effect of the structure of the sulfides on their reactivity. We were interested in studying the behavior of cyclic sulfides analogous to the sulfides in the middle fraction of petroleum, in reactions with benzoquinone and 5,8-quinolinedione. To this end we prepared sulfonium salts from sulfides IIa-j (see Table 1) and also made quantitative estimate of the reactivity of the sulfides by means of GLC. The composition and structure of the salts were proven by elementary analysis and IR and PMR spectroscopy.

During this, it was found that a basic feature of the sulfonium salts formed in reactions with 5,8-quinolinedione is that each molecule of the salt contains two anions of the acid. In the PMR spectra of these salts, a shift of the protons of the nitrogen-containing ring to weaker fields is observed, indicating the coordination of a second molecule of HCl per nitrogen atom of the heterocycle. This probably explains the fact that these salts when heated decompose at 150-180°C without melting. Physicochemical and spectroscopic methods have so far been unable to show unambiguously whether position 6 or 7 is joined to the sulfur.

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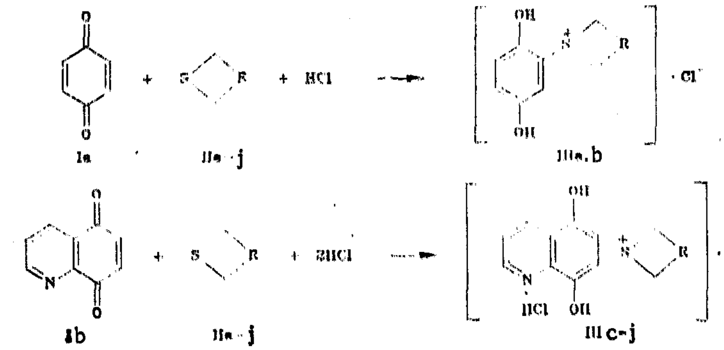
TABLE 1. The Relative Reactivities of the Sulfides

Compound	Sulfide	K_{rel} in reaction with:	
		1,4-benzoquinone	5,8-quinolinedione
IIa	Thiacyclopentane	1	1
IIb	3-Methylthiacyclopentane	0,70	0,67
IIc	2-Ethylthiacyclopentane	0,40	0,23
IId	2-Propylthiacyclopentane	0,27	0,19
IIe	2-Phenylthiacyclopentane	0,08	0,02
IIf	cis-2,4-Dimethylthiacyclohexane	0,52	0,27
IIg	trans-2,4-Dimethylthiacyclohexane	0,36	0,15
IIh	cis-2-Methyl-4-pentylcyclohexane	0,47	0,29
IIi	trans-2-Methyl-4-pentylcyclothiahexane	0,27	0,23
IIj	Concentrate of petroleum sulfides T_{boil} 210-230 °C	0,25	0,17



Earlier [3], we investigated the reaction of cyclic sulfides with quinoid-type compounds by measuring the redox potentials of the reaction medium. This method, however, gave only an approximate, qualitative estimation of the activity of the sulfides. In the present work, we used the method of concurrent reactions to estimate the relative reactivities quantitatively. The behavior of sulfides of the thiacyclopentane series was investigated along with a concentrate of petroleum sulfides in reactions with 1,4-benzoquinone and 5,8-quinolinedione. It follows from the results of the measurements, shown in Table 1, that unsubstituted thiacyclopentane has the highest reactivity. The introduction of methyl or other alkyl groups into the molecule reduces the activity of the sulfide. Apparently steric hindrance plays a decisive role because the extent of the reduction in reactivity is directly related to the size of the substitutent in the position α to the sulfur. In this process it has not been possible to observe any marked inductive, electron donor effect of the alkyl substituents accelerating the reaction. The least reactive is 2-phenylthiacyclopentane. In this case, apparently, the steric effect of the phenyl group further decreases the nucleophilicity of the sulfur atom because of the conjugation with the phenyl nucleus.

The introduction of a substituent in the 3-position, further removed from the sulfur atom, does not lead to a substantial change in the activity. Characteristically, the cis-dialkylthiacyclohexanes have a higher reactivity than the trans-isomers. This can also be explained by the greater accessibility of the sulfur atom in the cis-isomers to attack by the bulky quinone molecule.

Along with the individual sulfides, we submitted to the investigation a fraction (T_{boil} 210–230°C) of sulfide concentrate isolated by sulfuric acid extraction from the prebituminous fraction of a collection of southern Tadjik petroleum. From elementary analysis, the fraction contains 14% sulfur, which, for MW 200, means that the fraction of sulfur compounds in the concentrate comes to 85%. The concentrate consisted basically of mono- and bicyclic saturated sulfides. It was shown by desulfurization on Raney nickel in the vaporizer of a chromatograph that the concentrate contained primarily cyclic sulfides having alkyl substituents in the α-position to the sulfur. This apparently explains why the concentrate investigated showed a reactivity close to that of compounds having steric hindrance at the sulfur atom.

Comparing the order of activity of the sulfides in reactions with 1,4-benzoquinone and

TABLE 2

Compound	Initial compounds	Acid	T_{mp} (T_{bp}), °C	Found, %			Empirical formula	Calc., %		
				C	H	S		C	H	S
III a	Ia+IIa	HCl	119**			13,1	$C_{10}H_{13}ClSO_2$			13,8
III b	Ia+IIb	HCl	80			12,1	$C_{11}H_{15}ClSO_2$			12,9
III c	Ib+IIa	HCl	(155)	48,0	4,8		$C_{13}H_{14}NClSO_2 \cdot HCl$	48,9	4,7	
III d	Ib+IIb	HCl	(160)			9,6	$C_{14}H_{16}NClSO_2 \cdot HCl$			9,6
III e	Ib+IId	HCl	(160)	54,8	6,3		$C_{16}H_{20}NClSO_2 \cdot HCl$	55,2	6,0	
III f	Ib+IIk	HCl	(160)			7,9	$C_{19}H_{26}NClSO_2 \cdot HCl$			7,9
III g	Ib+IIa	H_2SO_4	(180)	34,8	4,3		$C_{13}H_{15}NS_2O_6 \cdot H_2SO_4$	35,2	3,8	
III h	Ib+IIb	H_2SO_4	(170)			20,0	$C_{14}H_{17}NS_2O_6 \cdot H_2SO_4$			21,0
III i	Ib+IIk	H_2SO_4	(190)			17,6	$C_{19}H_{27}NS_2O_6 \cdot H_2SO_4$			18,3
III j	I +IIa	HNO_3	(160)	42,3	4,1	8,0	$C_{13}H_{14}N_2SO_5 \cdot HNO_3$	41,8	4,0	8,6

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*IIk – 4-pentylcyclothiahexane.

†T_{mp} 119° [1].

5,8-quinolinedione, one can see that the deactivating effect of substituents in the thiacyclanes appears more clearly in the second case. According to the electronic theory of organic reactions, this is evidence of the lesser reactivity of 5,8-quinolinedione compared to 1,4-benzoquinone.

EXPERIMENTAL

Synthesis of Sulfonium Salts. To a solution of 10 mmoles of 1,4-benzoquinone or 5,8-quinolinedione and 10 mmoles of the sulfide in 15 ml of acetone at 0 to –2°C, we added, with stirring, a solution of acid (12 mmoles for 1,4-benzoquinone and 24 mmoles for 5,8-quinolinedione) in 5 ml of acetone. We used concentrated hydrochloric, concentrated nitric acid, or sulfuric acid diluted to 70% concentration with water. The salt precipitating out was filtered off, washed with cold acetone, dried, and analyzed. Yield, 50-80%. Elementary analyses and melting or decomposition points of some of the salts are shown in Table 2.

Procedure for the Concurrent Reactions and Calculation of K_{rel}. To run the concurrent reactions, we placed two or three sulfides in a 25-ml, two-necked flask with a stirrer and dropping funnel attached. The total amount of the sulfides came to 2.5 mmole. We added an inert compound (standard) and 5 ml of acetone. As standards, we used the hydrocarbons heptane, nonane, or decane. We then added 1.25 mmoles of 1,4-benzoquinone or 5,8-quinolinedine, cooled the mixture to a temperature of 0 to -2°C, and added 1.25 mmoles of concentrated HCl dropwise with stirring. We stirred at this temperature until the reaction was complete (30-40 min). We analyzed the mixture before and after the reaction in a Khrom-5 chromatograph; carrier gas, nitrogen; flame ionization detector; glass column, 2.5 m × 3 mm with SE-30 or OV-17 5% silicone on Chromaton. The immobile phase, thermostat temperature, and carrier gas flow rate depended on the specific mixture and were chosen to give the optimum separation of the sulfides and standard in the time of the analysis (10-15 min). We did not raise the temperature of the evaporator above 130°C in order to avoid decomposition of the salts which starts above 150°C, evolving volatile products (see Table 2). We determined the area of the peaks with an IT-2 electronic integrator (Czechoslovakia). In the investigation of the concentrate of petroleum sulfides, we used the sum of the areas of all the peaks of the compounds entering into the concentrate in the calculations.

We based the calculations of the relative rates of reaction on Eq. (1), which takes the form of Eq. (2) for analyses by GLC:

$$K_{rel} = \frac{\lg[C_I]_0 - \lg[C_I]}{\lg[C_{II}]_0 - \lg[C_{II}]}, \tag{1}$$

$$K_{rel} = \frac{\lg(S_I/S_{st})_0 - \lg(S_I/S_{st})}{\lg(S_{II}/S_{st})_0 - \lg(S_{II}/S_{st})}, \tag{2}$$

where K_{rel} is the ratio of the rate constant for the reaction of sulfide I to the rate constant the for reaction of sulfide II, $[C_I]_0$ and $[C_{II}]_0$ are the concentrations of sulfides I and II before the reaction; $[C_I]$ and $[C_{II}]$ are the concentrations of sulfides I and II after the reaction; $(S_I/S_{st})_0$ and $(S_{II}/S_{st})_0$ are the ratios of the areas of the chromatographic peaks of sulfide I to the standard and of sulfide II to the standard before the reaction; and (S_I/S_{st}) and (S_{II}/S_{st}) are the ratios of the areas of the chromatographic peaks of sulfide I to the standard and of sulfide II to the standard after the reaction.

Equation (2) is correct provided that the ratios $[C_I]/[S_I/S_{st})$ and $[C_{II}]/(S_{II}/S_{st})$ remain constant quantities over the range of concentrations studied. To fulfill this condition, we chose the concentrations of the reactants so that, in the GLC analyses, the peaks of the sulfides and the standard were comparable in area both before and after the reaction. To estimate the reproducibility of the determination of K_{rel}, we carried out several experiments to determine the relative activities of the same pairs of sulfides. In this way, we found that the error in the chromatographic results was no more than 2%, and in the value of K_{rel}, from 5 to 10%.

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PREPARATION OF SPIROAZIRIDINEFLUORENE, SPIROINDOXYLFLUORENE, AND β-AMINOPROPIONIC ACID ESTER WITH A 4-AZAFLUORENE FRAGMENT

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It has been established that the reaction of 9-(p-methoxyphenylimino)fluorene with dichlorocarbene (conditions of phase-transfer catalysis) proceeds in two directions — the formation of spiroaziridinefluorene and of spiroindoxylfluorene, the structure of which has been demonstrated. Opening of the aziridine ring of spiroaziridinefluorene has been accomplished. From the analagous azamethine, 4-aza-fluorene, an ester of N-substituted β-aminopropionic acid with a 4-azafluorene fragment was obtained by alkylation of its dianion with methyl chloroacetate.

The cycloaddition of carbenes to imines is widely used as a contemporary preparative method for the synthesis of aziridines [1]. There is no published information on the preparation of spiro compounds containing aziridine fragments from a series of fluorene imines by such a method. We have carried out a study of the compounds which are formed by the reaction of 9-(p-methoxyphenylimino)fluorene (I) with dichlorocarbene under phase-transfer catalysis conditions [2] using triethylbenzylammonium chloride (TEBA) as catalyst. The reaction does not proceed in only one direction. The main product is 3',3'-dichloro-1'-(p-methoxyphenyl)spiro-[aziridine-2',9-fluorene] (II) (75% yield). In addition to this, a compound with the composition $C_{21}H_{15}NO_2$ is obtained in 10% yield; spectroscopic data indicate that this is 5'-methoxyspiro[indoxyl-2',9-fluorene] (III). The structure of compound II is confirmed by carbon-13 NMR studies carried out during the present work. On heating the spiroaziridinefluorene II with ethanol (rectified spirit), opening of the aziridine ring occurs. In this way, 9-chloro-9-(N-p-methoxyphenylcarbamoyl)fluorene (IV) is obtained in quantitative

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