PREPARATION OF S-ARYLSULFONIACYCLANE SALTS

E. N. Karaulova, G. D. Gal'pern,
V. D. Nikitina, T. A. Bardina,
and L. M. Petrova

UDC 547.732'734

S-(4-Hydroxyaryl)sulfoniacyclane perchlorates have been obtained by the condensation of thiacyclanes with phenols in the presence of perchloric acid, phosphorus oxychloride, and hydrogen peroxide, or by condensing thiacyclane S-oxides under the same conditions but without the hydrogen peroxide. The capacity for forming sulfonium perchlorates decreases sharply in the sequence tetrahydrothiophene > thiacyclohexane > thiacycloheptane > methylthiacyclohexane; no sulfonium salts are obtained under these conditions from 2,2,6,6-tetramethylthiacyclohexane, 2-methyl-1-thiadecalin, or 2,5-dimethyltetrahydrothiophene. The S-(4-hydroxyaryl)sulfoniacyclane perchlorates take part in double-decomposition reactions, giving picrates, chlorides, and phosphates. The action of caustic potash in methanol on S-(4-hydroxyphenyl)tetrahydrothiophenium salt forms a dimeric sulfobetaine.

In the development of the chemistry of saturated cyclic sulfides, which are found in mineral oils [1], we undertook the synthesis of a number of sulfonium derivatives of thiacyclanes. Dialkylarylsulfonium salts have been obtained previously by condensing aromatic compounds having an activated para position with dialkyl sulfides in the presence of oxidizing agents and strong acids [2-4] or with the corresponding dialkyl sulfoxides in an acid medium [4-6]. We were the first to synthesize S-arylsulfoniacyclane salts [7]. Later, the production of S-phenyltetrahydrothiophenium and S-phenylsulfoniacyclohexane salts by the cyclodehydrohalogenation of ω-bromoalkyl phenyl sulfides in the presence of acetic anhydride and perchloric acid was reported. This method is suitable for the synthesis of simple S-phenylsulfoniacycloalkane perchlorates but does not offer the possibility of the direct use of the thiacyclanes that are characteristic for petroleum and petroleum products.

In order to obtain S-arylsulfoniacyclane salts, we used the method for the synthesis of dialkylarylsulfonium perchlorates [4]. By the condensation of phenol with tetrahydrothiophene, thiacyclohexane, and 2-methylthiacyclohexane in the presence of perchloric acid, phosphorus oxychloride, and hydrogen peroxide, and also with tetrahydrothiophene, thiacyclohexane, and thiacycloheptane S-oxides in the absence of hydrogen peroxide [7], and also by the reaction of tetrahydrothiophene and tetrahydrothiophene S-oxide with α-naphthol, we obtained S-(p-hydroxyaryl)sulfoniacyclane perchlorates (Table 1). The use of the S-oxides had no appreciable advantages over the use of the unoxidized cyclic sulfides and hydrogen peroxide. Under these conditions, cis- and trans-2,5-dimethyltetrahydrothiophene, 2,2,6,6-tetramethylthiacyclohexane, and 2-methyl-1-thiadecalin and the corresponding S-oxides do not react with phenols. In the case of thiacyclohexane and its S-oxide, in addition to the perchlorate, a sulfonium phosphate is formed in which the anion is the residue of a partially condensed form of phosphoric acid $H_2PO_4 \cdot H_4P_2O_7^-$ (see [9]).

Tetrahydrothiophene is distinguished by its high reactivity: the S-aryltetrahydrothiophenium perchlorates are formed in close to quantitative yields. The introduction of substituents into the α position interferes with the formation of the sulfonium salts to an extreme degree. In a number of cases, no reaction takes place: some sulfoxide is recovered unchanged while some of it is reduced to the sulfide; in addition chlorophenol is always formed as a result of the chlorination of the unchanged phenol by the phosphorus oxychloride.

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1479-1482, November, 1973. Original article submitted December 21, 1971.

TABLE 1. S-(Hydroxyaryl)sulfoniacyclane Salts

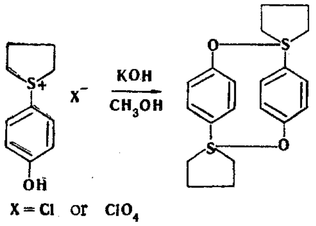
Sulfonium cation	Anion	mp, °C	Empirical formula	Found, %			Calc., %			Yield, % (method of synthesis)[a]
				C	H	Cl	C	H	Cl	
S-(p-Hydroxyphenyl)-tetrahydrothiophenium	Perchlorate	137—138	$C_{10}H_{13}ClO_5S$[b]	43,0	4,6	12,6	42,7	4,6	12,7	94 (A), 91 (B)
	Picrate	154—155	$C_{16}H_{15}N_3O_8S$	47,1	4,0		46,9	3,7		71 (C)
	Chloride	114—115	$C_{10}H_{13}ClOS$	55,4	6,0	16,3	55,4	6,2	16,3	74 (D)[c]
S-(4-Hydroxy-1-naphthyl)tetrahydrothiophenium	Perchlorate	184	$C_{14}H_{15}ClO_5S$	51,1	5,0	10,6	50,8	4,5	10,7	96 (A), 78 (B)
	Chloride	Oil	$C_{14}H_{15}ClOS \cdot H_2O$	59,8	6,0	12,1	59,2	6,8	12,3	93 (D)
	Picrate	172—177	$C_{20}H_{17}N_3O_8S$[e]	52,8	4,0		52,8	3,7		87 (C)[d]
S-(p-Hydroxyphenyl)-sulfoniacyclohexane	Perchlorate	154—158	$C_{11}H_{15}ClO_5S$[f]			11,8			12,0	19 (A), 50 (B)
	Phosphate[g]	105—107	$C_{11}H_{21}O_{12}P_3S$[h]	27,0	4,8		28,0	4,5		33 (A), 10 (B)
	Picrate[i]	180—181	$C_{17}H_{17}N_3O_8S$[j]							85 (C)
	Chloride	158—160	$C_{11}H_{15}ClOS$			14,9			15,4	91 (D)
S-(p-Hydroxyphenyl)-sulfoniacycloheptane	Perchlorate	172	$C_{12}H_{17}ClO_5S$	46,6	4,8	11,6	46,6	5,5	11,5	56 (A)
2-Methyl-1-(p-hydroxyphenyl)sulfoniacyclohexane	Perchlorate	Oil	$C_{12}H_{17}ClO_5S$			10,7			10,5	11 (A), 9 (B)
	Picrate	134—136	$C_{18}H_{19}N_3O_8S$[k]	49,0	4,6		49,4	4,4		70 (C)

a) Method of synthesis: A – condensation of phenol (or naphthol) with a thiacyclane S-oxide; B – condensation of phenol (or naphthol) with a thiacyclane; C – double decomposition of the perchlorate and picric acid; D – double decomposition of the perchlorate and potassium chloride. b) Found: S 11.4%. Calculated: S 11.4%. c) 4-Hydroxybutyl 4-hydroxyphenyl sulfide is formed simultaneously. d) Also obtained from the sulfonium chloride monohydrate. e) Found: N 8.8%. Calculated: N 9.2%. f) Found: S 10.9%. Calculated: S 10.9%. g) Isolated together with the perchlorate on synthesis by methods A and B. h) Found: P 19.4%. Calculated: P 19.8%. i) Also obtained from the phosphate, yield 78%. j) Found: N 9.7%. Calculated: N 9.5%. k) Found: N 9.3%. Calculated: N 9.3%.

In the salts obtained, the replacement of the anion takes place readily; this reaction confirms the structure of the compounds obtained as sulfonium salts (Table 1). When S-(p-hydroxyphenyl)tetrahydrothiophenium perchlorate was subjected to prolonged heating with an aqueous solution of potassium chloride, a small part of the sulfonium salt was converted with opening of the five-membered ring into 4-hydroxybutyl 4-hydroxyphenyl sulfide.

The structure of the sulfonium salts obtained as phenol and naphthol derivatives was confirmed by UV spectroscopy: the spectra of the S-(4-hydroxyphenyl)tetrahydrothiophenium, S-(4-hydroxyphenyl)sulfoniacyclohexane, and S-(4-hydroxyphenyl)methylsulfoniacyclohexane perchlorates each had a single absorption band in the 245-250-nm region which is characteristic for phenol derivatives; the UV spectrum of S-(4-hydroxy-1-naphthyl)tetrahydrothiophenium had maxima at 236 and 315 nm, which are characteristic for α-naphthol derivatives.*

When S-(p-hydroxyphenyl)tetrahydrothiophenium perchlorate or chloride was treated with a solution of caustic potash in methanol, it was impossible to isolate the sulfonium base from the reaction mixture: apparently, when the filtrate (after the elimination of the potassium salts) was concentrated the condensation of two molecules of the sulfonium base took place with the elimination of water and the formation of a peculiar very sparingly soluble sulfobetaine the IR spectrum of which lacked the absorption band of a hydroxy group.



EXPERIMENTAL

The UV spectra of the sulfoniacyclane perchlorates were obtained on an EPS-3T spectrophotometer in aqueous solutions.

S-(p-Hydroxyphenyl)tetrahydrothiophenium Perchlorate. A. To 26 ml of 67% perchloric acid was added 20 ml of phosphorus oxychloride and then, with ice cooling, 4.7 g (0.05 mole) of phenol, followed at a temperature of the reaction mixture of 0-5°C by 5.2 g (0.05 mole) of tetrahydrothiophene S-oxide (containing 29.2% of sulfoxide sulfur). The mixture was kept at 0°C for 4 h and then at room temperature for 12 h and was poured on an ice; the S-(4-hydroxyphenyl)tetrahydrothiophenium perchlorate that deposited (see Table 1) was suitable without further purification for subsequent use. For analysis it was crystallized from water or dilute ethanol.

B. With ice cooling, 9.6 g of phosphorus oxychloride, 2.35 g (0.025 mole) of phenol, and 2.2 g (0.025 mole) of tetrahydrothiophene were added to 21.3 g of 67% perchloric acid. With ice–salt cooling, 2.5 g of 34% hydrogen peroxide (0.025 mole) was added at such a rate that the temperature of the mixture was between −2 and +8°C. Then the S-(4-hydroxyphenyltetrahydrothiophenium perchlorate was isolated as described above.

The other sulfoniacyclane perchlorates (see Table 1) were obtained similarly.

S-(p-Hydroxyphenyl)sulfoniacyclohexane Phosphate. After the isolation of S-(4-hydroxyphenyl)sulfoniacyclohexane perchlorate, prepared from thiacyclohexane S-oxide, an excess of a saturated solution of sodium chloride was added to the filtrate, the potassium perchlorate was separated off, and the filtrate was concentrated at 100°C and was extracted with isobutanol with heating. The ethanol was distilled off in vacuum, the residue was dissolved in acetone, and the solution was diluted with ether. The phosphate that deposited was purified by boiling its aqueous solution with activated carbon (see Table 1).

1-(p-Hydroxyphenyl)-2-methylsulfoniacyclohexane Perchlorate. In the case of 2-methylthiacyclohexane, after the end of the reaction the mixture was poured onto ice; the oil was separated off, washed

---

*The UV spectra were obtained by N. A. Shimanko (A. V. Topchiev Institute of Petrochemical Synthesis of the Academy of Sciences of the USSR).

with benzene, and extracted with isobutanol. The extract was washed from acid, and after the solvent had been distilled off in vacuum S-(4-hydroxyphenyl)-2-methylsulfoniacyclohexane perchlorate was obtained (see Table 1).

S-(p-Hydroxyphenyl)tetrahydrothiophenium Chloride and 4-Hydroxybutyl 4-Hydroxyphenyl Sulfide. A mixture of 2.8 g (0.01 mole) of S-(4-hydroxyphenyl)tetrahydrothiophenium perchlorate and 34 ml of saturated aqueous potassium chloride was boiled for 13 h. On cooling, potassium perchlorate precipitated, and after its separation the 4-hydroxybutyl 4-hydroxyphenyl sulfide was extracted from the filtrate with ether or benzene and was then recrystallized from benzene; yield 3.5% (when the perchlorate was boiled with a solution of potassium chloride for 30 h, the yield of sulfide was 16%). mp 67°C. Found: C 60.8; H 7.0%. $C_{10}H_{14}O_2S$. Calculated: C 60.6; H 7.1%.

The aqueous solution after the separation of the sulfide was evaporated to dryness and, with heating, isobutanol was extracted from the residue the S-(4-hydroxyphenyl)tetrahydrothiophenium chloride, which was recrystallized from a mixture of ethanol and acetone (1:1) (see Table 1). The other sulfoniacyclane chlorides (Table 1) were obtained similarly.

Sulfobetaine from S-(p-Hydroxyphenyl)sulfoniacyclane Salts. Solutions of 2.8 g (0.01 mole) of S-(4-hydroxyphenyl)tetrahydrothiophenium perchlorate in 15 ml of methanol and of 0.56 g (0.01 mole) of caustic potash in 12 ml of methanol were mixed and boiled for 6 h. After cooling, the potassium perchlorate was filtered off, the filtrate was evaporated, and the residue was washed with water and acetone from starting materials that had not reacted (yield 70%). The sulfobetaine was obtained similarly from S-(4-hydroxyphenyl)tetrahydrothiophenium chloride (yield 48%). Solubility at 20°C in water 0.008%, in ethanol and acetone ~0.1%. mp 150-151°C. Found: C 66.0; H 7.1%; mol. wt. 357 (cryoscopy in camphor according to Rast). $C_{20}H_{40}O_2S_2$. Calculated: C 66.6; H 6.7%; mol. wt. 360.

LITERATURE CITED

1. E. Karaulova, The Chemistry of the Sulfides of Petroleum [in Russian], Nauka, Moscow (1970), p. 35.
2. W. S. MacGregor, Crown Zellerbach Corp., French Patent No. 1,348,846 (1964); Chem. Abstr., 61, 4271 (1964).
3. Crown Zellerbach Corp., British Patent No. 987,810 (1963).
4. S. Ukai and K. Hirose, Chem. Pharm. Bull. (Tokyo), 16, 606 (1968).
5. K. Wedemeyer and D. Delfs, German Federal Republic Patent No. 1,088,980 (1960); Chem. Abstr., 55, 25863 (1961).
6. E. Goethals and P. de Radzitzky, Bull. Soc. Chim. Belge, 73, 546 (1964).
7. E. N. Karaulova, USSR Author's Certificate No. 327,189; Byul. Izobret., No. 5, 67 (1972).
8. S. Oae, W. Furukawa, I. Jano, T. Aida, and H. Kobayashi, Third Intern. Congress of Heterocycl. Chem. Abstracts of Contributed Papers. The Tohoku University, Sendai, Japan, 616 (1971).
9. L. V. Kubasova, Usp. Khim., 40, 3 (1971).