CHEMISTRY OF TRIMETHYLENE OXIDE

COMMUNICATION 1. cis- AND trans-7-OXABICYCLO[4.2.0]OCTANE

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In 1938 Rupe and Klemm [1] prepared 7-oxabicyclo[4.2.0]octane (V, VII) from 2-hydroxycyclohexanemethanol (I, II), which was prepared by the catalytic reduction of 2-(hydroxymethylene)cyclohexanone. 2-Hydroxycyclohexanemethanol was treated with sulfuric acid in ethanol solution, and the resulting oxetane derivative was purified with the aid of its ferrocyanide complex. From 25 g of the diol 1.3 g of the oxetane derivative was prepared. Later, Mousseron and co-workers [2] showed that the 2-hydroxycyclohexanemethanol obtained by Rupe and Klemm is a mixture of two isomers (95% and 5%). The cis and trans configurations of (I) and (II) were determined by Siegel [3], who brought the two isomers into configurative relation with cis- and trans-2-hydroxycyclohexanecarboxylic acids of known configuration [4] and with cis- and trans-2-methylcyclohexanols [5-8].

The cis modification (I) of 2-hydroxycyclohexanemethanol, which was required for our experiments, was prepared by the method of Mannich and Brose [9] and Mousseron [2], and for the preparation of the trans compound (II) we used Matti's method with some modifications. The stereospecificity of Prince's reaction, described by Matti, and the trans configuration of the final product were proved by Fodor and co-workers [11], and also by Smissmann and co-workers [12].

The ring-closure reaction carried out by Rupe and Klemm [1] was found to be inconvenient for our purposes. Methods used for the preparation of 1,3-chlorohydrins and 1,3 chloro acetates [13,14] could not be regarded as suitable either because, for example, the preparation of the halohydrin with the aid of hydrochloric acid or hydrogen bromide [15], and also the reaction with acetyl chloride, gives a mixture of primary and secondary halogen derivatives of variable composition [16,17]. With phosphorus pentachloride a dihalo derivative was obtained [2], and with thionyl chloride a cyclic sulfinic ester [19]. By introducing some modifications into Siegel's method [3], we succeeded in preparing crystalline cis- and trans-(2-hydroxycyclohexyl)methyl p-toluenesulfonates (III) and (IV); cis, m.p. 59°; trans, m.p. 75-76° (Siegel gives: cis, an oil; trans, m.p. 75.5-76.5°).

For β-epoxy ring closure, the cis and trans monotoluenesulfonic esters (III) and (IV) were dissolved in ether and then added dropwise to concentrated potassium hydroxide solution in a flask situated in an oil bath at 150-160° with simultaneous passage of steam through the reaction mixture. In the case of the cis compound (III) we obtained a single product (58%) with a characteristic smell and an empirical formula of $C_7H_{12}O$ (V); it contained almost no active hydrogen. In its infrared spectrum there was an intense absorption band in the region of 950 cm^{-1}, characteristic for cyclic esters [20-22]. In the regions of 1730 and 3060 cm^{-1} there was also some absorption. By fractional distillation we isolated 2-methylenecyclohexanol (VI) (7%), which was identified by analysis and by the preparation of its p-nitrobenzoate (m.p. 62°).

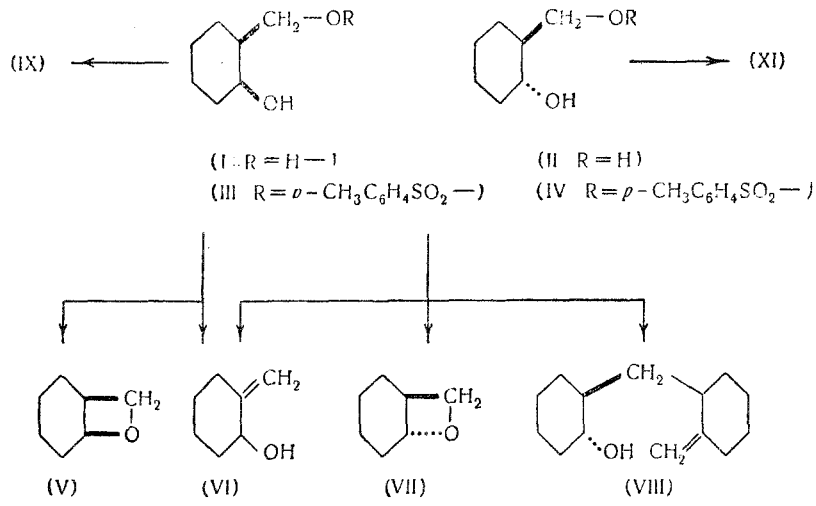
The products of the cyclization of trans-(2-hydroxycyclohexyl)methyl p-toluenesulfonate (VI) (yield of crude distillate 58%) were subjected to fractional distillation, and three different substances were obtained. The first fraction (14.2%) was again found to be a substance of empirical formula $C_7H_{12}O$. In the infrared spectrum of this compound there appeared an intense absorption band [20-22] in the region of 950 cm^{-1} and weaker bands in the regions of 1640, 1730, and 3080 cm^{-1}. The second fraction (12.7%) was found to be mainly 2-methylenecyclohexanol (VI), and the third fraction (21.8%), on the basis of analysis and molecular weight determination, was a dimeric product of formula $C_{14}H_{24}O_2$ which, on the basis of microhydrogenation data, active-hydrogen determination and analysis of its 3,5-dinitrobenzoate, may be described with great probability by formula (VIII). A synthesis that proves the structure (VIII) is being carried out.

Substance	Rf	Color of spot	Full development of color	M. p., °C	Analysis, calculated for $C_{17}H_{29}O_4NS$	
					found %	calc. %
(IX)	0.49	Orange	5 hr	143	59.25	59.44
					8.50	8.51
(X)	0.57	Yellowish-violet	quickly	188	59.69	59.44
					8.40	8.51
(XI)	0.54	Orange	5 hr	196	59.62	59.44
					8.62	8.51
(XII)	0.58	Yellowish-violet	quickly	157	59.60	59.44
					9.45	8.51

The formation of 2-methylenecyclohexanol (VI) is to be explained by an E2 mechanism, and is a reaction competing with the intramolecular S_N2 process leading to the formation of the oxetane rings of (V) and (VII). In the case of the trans compound (IV), the S_N2 process gives an oxetane derivative in lower yield (V, 58%; VII, 14.2%) because of unfavorable spatial conditions. The dimeric product (VIII) is probably formed by the reaction between trans-(2-hydroxycyclohexyl)methyl p-toluenesulfonate (IV) and 2-methylenecyclohexanol (VI) by bimolecular nucleophilic substitution.

To prove the cis and trans configurations of the two isomeric 7-oxabicyclo[4.2.0]octanes, both (V) and (VII) were treated at room temperature in dry ether with p-toluenesulfonic acid, and the product was then caused to react with trimethylamine. Analysis, carried out with the aid of paper chromatography, showed the presence among the products of the transformations of the cis and trans forms of 7-oxabicyclo[4.4.2] octane of two substances from each form (see table).

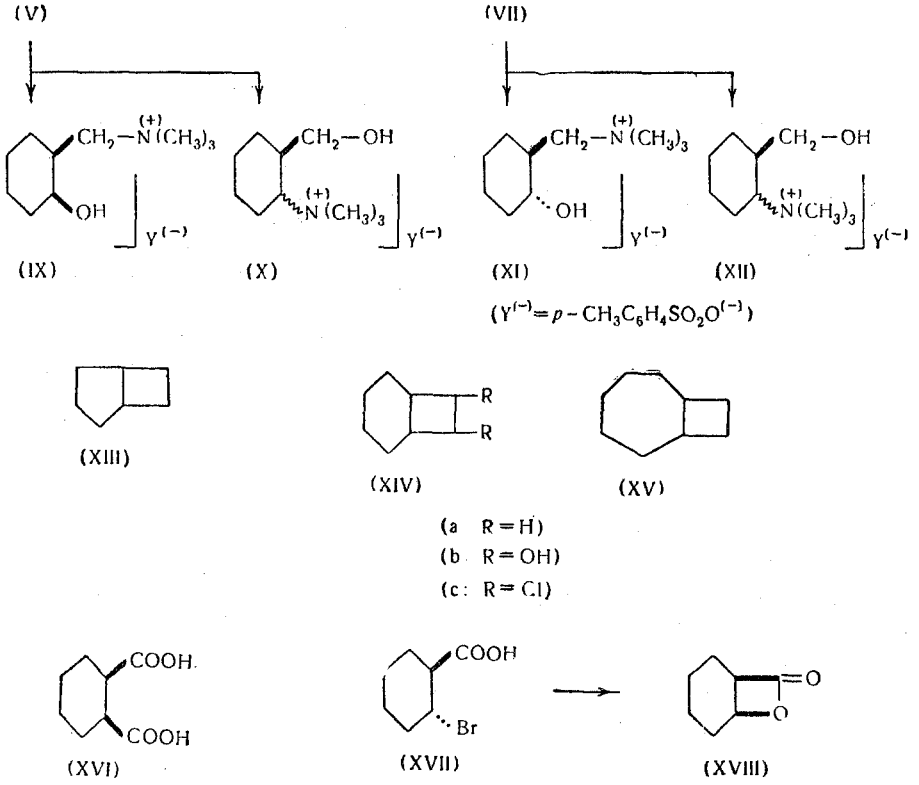
After two crystallizations from ethanol, both mixtures gave the same two substances (X) and (XII), which differed from (IX) and (XI), obtained directly from (III) and (IV), in melting point and value of Rf. Hence, under the attack of the nucleophilic p-toluenesulfonate anion, cis- and trans-7-oxabicyclo[4.2.0]octanes (V) and (VII) evidently formed in each case two different (primary and secondary) monotosylates, which were converted under the action of trimethylamine into quaternary ammonium salts, which could be produced as a result of the addition of amines to a primary (IX and XI) and to a secondary (X and XII) carbon atom. The configurations of (X) and (XII) require further proof.



On the basis of our appraisal of the above-described ring-opening reaction, and also on the basis of data of analytical and spectroscopic investigations, the existence of the trans isomer (VII) in addition to cis-7-oxabicyclo-[4.2.0]octane (V) appears to be quite acceptable. The formation of this compound with high internal strain is worthy of attention from the stereochemical and energetic points of view because no bicyclic compound with trans[4.4.2] annelation has been described previously, either among carbocyclic or among heterocyclic compounds. The very small difference [23] between the lengths of the C – C and C – O bonds (1.54 and 1.44 A), and also between the

valence angles of C – C – C and C – O – C (109° and 110°) permits us to make a comparison between derivatives of bicyclo[4.2.0]octanes, which belong to the carbocyclic series, and derivatives belonging to the heterocyclic series. The cis configuration of the compounds described is proved by the formation of bicyclo[4.2.0]octane [24], by the decomposition of its dihydroxy derivative (XIVb) into cis-1,2-cyclohexanedicarboxylic acid (XVI), and also by the increase in the stability of the cyclobutane ring [25] on hydrogenation of the dichloro derivative (XIVc). The supposed lactone (XVIII), which is assumed to be a derivative of 7-oxabicyclo[4.2.0]octane, also has cis annelation in view of the mechanism of the reaction (XVII) → (XVIII) [26]. The easier formation and higher yield of the cis modification (V) (cis, 58%; trans, 14.2%) appears to prove the higher stability of the cis compound, as compared with the trans compound (VII). According to Allinger and co-workers [27, 28], if a second ring is fused in the 1,2-position to cyclobutane (XIII, XIV, and XV), in the case of a ring with a greater number of members (XV), the trans modification will probably have the lower heat content: "where in the series indicated, (XIII), (XIV), (XV), the intersection point will be found it is impossible to predict unequivocally." On the basis of conclusions reached by us as a result of ring-closure reactions, it may be supposed that in the series of bicyclic compounds containing the trimethylene oxide ring the intersection may occur only in the case of a pair of compounds containing more carbon atoms than 7-oxabicyclo-[4.2.0]octane. Investigations starting from 2-hydroxycycloheptanemethanol monotosylates are being carried out.

In the future, by determining the dipole moments of the isomers (V) and (VII) we shall attempt to apply to cis- and trans-7-oxabicyclo[4.2.0]octanes Allinger's conformational rule [27,28], according to which, for cyclic stereoisomers having identical dipole moments, that isomer has the least enthalpy for which the molecular volume is the least, i.e., the boiling point, density, and refractive index are lower. A positive result in the application of the conformational rule would confirm our conclusions made on the basis of the conditions for the formation of 7-oxabicyclo[4.2.0]octane. The higher stability of the cis isomer (V) may be interpreted also on the basis of the conformational relations of the two isomers. The trimethylene oxide ring may be regarded as planar [29]. From this it follows that the directions of the valences of the carbon atoms common to both rings have a shielded conformation in the trimethylene oxide ring. It follows that in the cyclohexane skeleton of the cis isomer (V) the strain is less than in the cyclohexane skeleton of the trans isomer (VII) [30], for, in order to make the equatorial-equatorial substituents of cis-(2-hydroxycyclohexyl)methyl p-toluenesulfonate (III) that participate in ring formation occupy a coplanar position very much less energy is required (the axial H atoms are remote from each other) than in the case of the equatorial trans compound (IV), which contains equatorial substituents (the axial H atoms are close to each other). According to electron diffraction measurements, 1,2-epoxycyclohexane has a half-chair conformation [31], so that it is probable that the cyclohexane ring of cis-7-oxabicyclo[4.2.0]octane (V) is also in a half-chair and not boat conformation.



When our experiments had been completed, we learned of the work of Henbest and Millward [22], who prepared cis- and trans-(2-hydroxycyclohexyl)methyl bromobenzenesulfonates. From the cis compound, under the action of potassium t-butoxide, they prepared a derivative of the oxetane (V) in 67% yield, but from trans-(2-hydroxycyclohexyl)methyl p-bromobenzenesulfonate, apart from a little (14%) of trans-2-(butoxymethyl)cyclohexanol, they obtained only a polymeric product. The formation of trans-7-oxabicyclo[4.2.0]octane, as described in this paper, is explained by the milder reaction conditions.

Apart from the above-described experiments, we carried out also the preparation and study of saturated and unsaturated trimethylene oxide derivatives condensed with carbocycles and heterocycles having various numbers of members.

The results obtained in the solvolysis of cis- and trans-2β-(chloromethyl)-3β-tropanol acetate [32], which was effected with sodium acetate in glacial acetic acid, permit us to conclude that also in the solvolysis of cis- and trans-(2-acetoxycyclohexyl)methyl p-toluenesulfonates the ring-opening of the acetoxonium ion [33-34] formed as an intermediate product would give a mixture of cis- and trans-2-hydroxycyclohexanemethanol diacetates. We are studying this question.

EXPERIMENTAL

2-(Hydroxymethyl)cyclohexanone. This was prepared from 980 ml (10.0 moles) of cyclohexanone by Mannich and Brose's method [9]. Refractionation gave 170 g (13.07%) of pure 2-(hydroxymethyl)cyclohexanone; b.p. 114-118° (16 mm); $n^{20}D$ 1.4792.

cis-2-Hydroxycyclohexanemethanol (I). 2-(Hydroxymethyl)cyclohexanone (52 g; 0.4 mole) was hydrogenated in methanol (200 ml) over Raney nickel (20 g) under a pressure of 72 atm [2]. The oil obtained after the treatment (49.5 g) was fractionated. The main fraction (36.5 g) had b.p. 143-146° (7 mm) and $n^{25}D$ 1.4871; after recrystallization from ether: m.p. 51° (27.5 g; yield 53%). Found: C 64.80; H 10.77%. $C_7H_{14}O_2$. Calculated: C 64.58; H 10.84% [3]; p-nitrobenzoate, m.p. 134° [11].

A mixture of 16.45 g (0.12 mole) of cis-2-hydroxycyclohexanemethanol (I) and 19.0 g (0.12 mole) of p-nitrobenzaldehyde dissolved in 65 ml of absolute ethanol was boiled in presence of 0.5 ml of concentrated sulfuric acid for 3 hr. On cooling there separated 26.7 g (81%) of the p-nitrobenzylidene derivative as light-green crystals. After recrystallization from ethanol we obtained 20.9 g (66%) of pure product; m.p. 82-84°; the melting point of a mixture with the corresponding trans isomer was 57-59°. Found: C 64.06; H 6.44%. $C_{14}H_{17}O_2N$. Calculated: C 63.84; H 6.54%.

trans-2-Hydroxycyclohexanemethanol (II). A mixture of the mono- and di-acetates of trans-2-hydroxycyclohexanemethanol was converted into the corresponding diol by Zemplen's deacylation method [35]. trans-2-Hydroxycyclohexanemethanol (II) had b.p. 105-110° (3 mm); yield 38.2%. Found: C 64.98; H 10.72%. $C_7H_{14}O_2$. Calculated: C 64.58; H 10.84%. p-Nitrobenzoate, m.p. 98° [11]. After crystallization from ethanol, the nitrobenzylidene derivative melted at 82°; the melting point of a mixture with the corresponding cis isomer was 56-59°. Found: C 64.20; H 7.02%. $C_{14}H_{17}O_2N$. Calculated: C 63.84; H 6.54%.

cis-(2-Hydroxycyclohexyl)methyl p-Toluenesulfonate (III). At 0° a solution of 16.06 g (0.08 mole) of p-toluenesulfonyl chloride in 50 ml of dry pyridine was added in small portions to a solution of 10 g (0.077 mole) of cis-2-hydroxycyclohexanemethanol (I) in 20 ml of dry pyridine. The reaction mixture was then left for 1 day at room temperature. The pyridine hydrochloride that separated was filtered off; the solution was extracted with chloroform, and the extract was washed with water, with 3N HCl, and again with water. After drying and removal of solvent, there remained a yellowish oily product, which crystallized out after several hours. Three crystallizations from ether gave pure cis-(2-hydroxycyclohexyl)methyl p-toluenesulfonate (III) (17.1 g; 78.4%); m.p. 59°. Found: C 59.19; H 6.99%. $C_{14}H_{20}O_2S$. Calculated: C 59.12; H 7.05% [3].

cis-[(2-Hydroxycyclohexyl)methyl]trimethylammonium p-Toluenesulfonate (IX). (2-Hydroxycyclohexyl)methyl p-toluenesulfonate (III) (1 g; 0.0035 mole) was dissolved in 20 ml of a benzene solution of trimethylamine (trimethylamine content 5.2%); the reaction mixture was then kept in a sealed tube at 80° for 10 hr. On cooling, the quaternary salt was precipitated, and was filtered off, washed with ether, and then recrystallized from a mixture of ether and ethanol; m.p. 143°; yield 1.02 g (85.1%). Found: C 59.25; H 8.50%. $C_{17}H_{29}O_4S$. Calculated: C 59.44; H 8.51%.

trans-(2-Hydroxycyclohexyl)methyl p-Toluenesulfonate (IV). By the method described for the preparation of

the cis compound (III), from 10 g (0.077 mole) of trans-2-hydroxycyclohexanemethanol (II) we obtained, after three crystallizations from ether, 14.3 g of pure trans-(2-hydroxycyclohexyl)methyl p-toluenesulfonate (IV) (66%; m.p. 75 to 76°). Found: C 59.35; H 6.70%. $C_{14}H_{20}O_4S$. Calculated: C 59.12; H 7.05% [3].

trans-[(2-Hydroxycyclohexyl)methyl]trimethylammonium p-Toluenesulfonate (XI). By the method described for the preparation of the cis compound (IX) we obtained 0.83 g (69%) of the pure trans quaternary ammonium salt (XI), m.p. 196°. Found: C 59.62; H 8.62%. $C_{17}H_{29}O_4S$. Calculated: C 59.44; H 8.51%.

cis-7-Oxabicyclo[4.2.0]octane (V). A one-liter, three-necked flask fitted with dropping funnel, tube for the passage of steam, and still-head was charged with a solution of 200 g of potassium hydroxide in 100 ml of water. The flask was placed in an oil bath at 150-160°, and steam was passed in vigorously while dropwise addition was made over a period of 50 min of a solution of 120 g (0.425 mole) of (2-hydroxycyclohexyl)methyl p-toluenesulfonate (III) in 560 ml of ether. The ether layer was then separated from the aqueous layer, and the latter was extracted with ether. The ether extracts were combined and dried over sodium sulfate; ether was then distilled off from a water bath. The residue was a liquid of characteristic odor (36 g; 72%). The oil obtained in two experiments (73 g) was fractionated through a 25-cm column containing a glass-spiral filling. According to its analysis, the main fraction [55.5 g, 58%; m.p. 75° (29); $n^{24}D$ 1.4642; d^{24}_4 0.9692] consisted of cis-7-oxabicyclo[4.2.0]octane (V). Found: C 75.04; H 10.37%; mol. wt. 112.0. $C_7H_{12}O$. Calculated: C 74.94; H 10.77%; mol. wt. 112.17. Its infrared spectrum contained a strong absorption band at about 950 cm^{-1} and weaker bands at about 1730 and 3060 cm^{-1}. The succeeding fraction was redistilled, and we obtained 6.7 g (7%) of 2-methylenecyclohexanol (VI); b.p. 184° (760 mm), $n^{20}D$ 1.4843. Found: C 75.10; H 10.62%. On microhydrogenation, one molecular proportion of hydrogen added; active hydrogen 0.83%. For $C_7H_{12}O$, calculated C 74.94; H 10.77, active hydrogen 0.80%; p-nitrobenzoate, m.p. 62°. Found: C 64.18; H 5.52%. $C_{14}H_{15}O_4N$. Calculated: C 64.34; H 5.30%.

Analogous results were obtained when 14 g of cis-(2-hydroxycyclohexyl)methyl p-toluenesulfonate (III) was mixed with 4 g of finely ground potassium hydroxide and the flask containing the mixture was heated in an oil bath at 140-160° for 20 min. Vacuum distillation gave 3.2 g (58%) of cis-7-oxabicyclo[4.2.0]octane.

trans-7-Oxabicyclo[4.2.0]octane (VII). This was prepared from 120 g (0.425 mole) of trans-(2-hydroxycyclohexyl)methyl p-toluenesulfonate (IV) by the method described for the cis modification. The only difference was that the duration of the reaction was 100 min. From the distillate we isolated 28 g (58%) of a liquid of characteristic odor. The oil obtained in two experiments (55 g) was fractionated through a 25-cm column.

Fraction I: 13.5 g, 14.2%; b.p. 157-158° (760 mm); $n^{18}D$ 1.4598. Found: C 74.85; H 10.62%; mol. wt. 112.0. $C_7H_{12}O$. Calculated: C 74.94; H 10.77%; mol. wt. 112.17. The infrared spectrum contained a strong absorption band at about 950 cm^{-1} and weaker bands at about 1640, 1730, and 3080 cm^{-1}. These data indicate the presence of trans-7-oxabicyclo[4.2.0]octane (VII). Fraction II: 12.0 g, 12.7%; b.p. 184° (760 mm); $n^{20}D$ 1.4843. Found: C 75.05; H 10.58%; on microhydrogenation one molecular proportion of hydrogen added; active hydrogen 0.82%. Calculated for $C_7H_{12}O$: C 74.94; H 10.77%; active hydrogen 0.803%; p-nitrobenzoate, m.p. 72°. Found: C 64.24; H 5.44%. $C_{14}H_{15}O_4N$. Calculated: C 64.34; H 5.30%. According to these data, Fraction II was 2-methylenecyclohexanol (VI). Fraction III: 20.7 g, 21.8%; b.p. 156-158° (3 mm); $n^{21}D$ 1.4958. Found: C 75.10; H 10.48; mol. wt. 225.0; on microhydrogenation one molecular proportion of hydrogen added; active hydrogen 0.50%. For $C_{14}H_{24}O_2$, calculated C 74.94; H 10.77%; mol. wt. 224.33; active hydrogen 0.44%; 3,5-dinitrobenzoate, m.p. 73-74°. Found: C 60.65; H 6.10%. $C_{21}H_{26}O_7N_2$. Calculated: C 60.25; H 6.26%. According to these data, the substance contained in Fraction III is, in all probability, to be represented by formula (VIII).

Reaction of cis-7-Oxabicyclo[4.2.0]octane (V) with p-Toluenesulfonic Acid and Reaction of the Product Formed with Trimethylamine. cis-7-Oxabicyclo[4.2.0]octane (1 g, 0.008 mole) was dissolved in dry ether (25 ml), and then p-toluenesulfonic acid (1.54 g; 0.008 mole) was added. The reaction mixture was stirred for 5 hr at room temperature and was then left to stand overnight. The ethereal solution was shaken with 5 ml of dilute sodium bicarbonate solution, dried over sodium sulfate, and then evaporated. The thick, slightly brown oily residue (2.34 g) was dissolved in 30 ml of a benzene solution of trimethylamine (trimethylamine content 5.2%); the reaction mixture was heated in a sealed tube for 10 hr at 75-80°. After cooling, the mixture of quaternary salts formed (1.96 g) was filtered off, washed with ether, and crystallized twice from ethanol; m.p. 188°. Found: C 59.69; H 8.40%. $C_{17}H_{29}O_4NS$. Calculated: C 59.44; H 8.51%. According to analysis by paper chromatography, the recrystallized product was an individual compound. The R_f of the spot obtained was 0.57, and it was yellowish violet in color; on the other hand, the crude product gave two clearly defined spots of different color when developed with Dragendorf's reagent; R_f 0.57 and 0.49. The R_f and color of the second spot (0.49) were identical to the R_f and developed color of cis-[(2-hydroxycyclohexyl)methyl]trimethylammonium p-toluenesulfonate (IX) obtained directly from (III) (0.49, orange).

On the basis of the data cited, the substance isolated from the mixture was very probably cis- or possibly trans-[2-(hydroxymethyl)cyclohexyl]trimethylammonium p-toluenesulfonate (X).

Reaction of trans-7-Oxabicyclo[4.2.0]octane (VII) with p-Toluenesulfonic Acid and Reaction of the Product Formed with Trimethylamine. Starting with 1 g (0.008 mole) of trans-7-oxabicyclo[4.2.0]octane (VII), we carried out the reaction in the way described for the case of the cis compound. After reaction with trimethylamine we obtained 1.52 g of a mixture of quaternary salts which, after two crystallizations from ethanol, melted at 157°. Found: C 59.60; H 8.45%. $C_{17}H_{29}O_4NS$. Calculated: C 59.44; H 8.51%. The individual character of the recrystallized product was proved by analysis, which was carried out with the aid of paper chromatography. The R_f of the spot obtained was 0.58, and its color was yellowish violet; on the other hand, the crude product gave two clearly defined spots of different colors when developed with Dragendorf's reagent; R_f 0.58 and 0.54. The R_f and color of the second spot (0.54) were identical to the R_f and developed color of trans-[(2-hydroxycyclohexyl)methyl]trimethylammonium p-toluenesulfonate (XI) obtained directly from (IV) (0.54, orange). On the basis of these data, the substance isolated from the mixture was very probably trans- or possibly cis-[2(hydroxymethyl)cyclohexyl]trimethylammonium p-toluenesulfonate (XII).

Analytical Procedure with the Aid of Paper Chromatography. We carried out down-flow chromatography at 20°, using Whatman No. 1 paper. The paper was impregnated twice with a 6:1 mixture of 6 N HCl and 1 N ammonium chloride; 130 γ of mixtures of quaternary salts were applied to the paper; authentic (IX) and (XI) were applied, and also the compounds (X) and (XII) isolated from the mixtures (75 γ each). The chromatography was carried out over a period of 36 hr with an 8:1:1 mixture of butyl alcohol, 2 N HCl, and water. In development with Dragendorf's reagent, various rates of development and colors of spots were obtained (see table).

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SUMMARY

The cis and trans modifications of 7-oxabicyclo[4.2.0]octane were prepared. The structures of both isomers were proved on the basis of infrared spectrum investigations and of derivatives obtained as a result of ring opening under the action of p-toluenesulfonic acid.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
