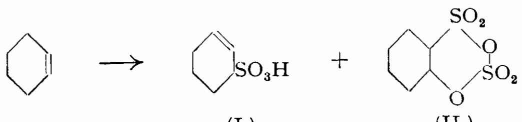
410. *Reactions of Cyclic Hydrocarbons. Part I. The Sulphonation of* cyclo*Hexene and* 1-*Methyl*cyclo*pentene.**

By R. Sperling.

Sulphonation of *cyclo*hexene with the dioxan–sulphur trioxide complex gave *cyclo*hexene-3-sulphonic acid and anydro-*trans*-2-sulpho*cyclo*hexyl hydrogen sulphate, whereas 1-methyl*cyclo*pentene gave 1-methyl*cyclo*pentene-5-sulphonic acid and some unsaturated disulphonic acids.

THE sulphonation of olefins by means of dioxan–sulphur trioxide complex suspended in ethylene dichloride has been extensively investigated by Suter and his collaborators (*J. Amer. Chem. Soc.*, 1938, **60**, 538; 1941, **63**, 978, 1594; 1943, **65**, 507; 1944, **66**, 1105; 1945, **67**, 827). According to the nature of the olefin, they obtained unsaturated sulphonic acids or sulphated hydroxysulphonic acids, the reaction being accompanied by little polymerisation or other side-reactions.

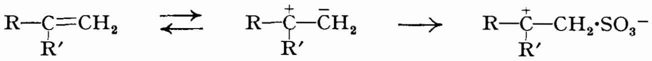
Such treatment of *cyclo*hexene resulted in the formation of *cyclo*hexene-3-sulphonic acid (I) as principal product, which was accompanied by anhydro-*trans*-2-sulpho*cyclo*hexyl hydrogen sulphate (II) and a small amount of similar derivatives from the dimer, *cyclo*hexenyl*cyclo*hexane.



(I.) (II.)

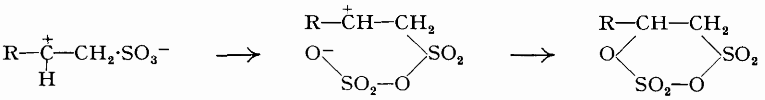
1-Methyl*cyclo*pentene, which can be regarded as a possible isomerisation product of *cyclo*hexene (cf. Block and Thomas, *J. Amer. Chem. Soc.*, 1944, **66**, 1589), gave 1-methyl*cyclo*pentene-5-sulphonic acid with some unsaturated disulphonic acids, whilst no anhydro sulphated hydroxysulphonic acids were produced. 1-Methyl*cyclo*pentene-5-sulphonic acid was much less stable than *cyclo*hexene-3-sulphonic acid, the carbon–sulphur bond being readily ruptured. This instability is probably due to the increased strain introduced into the five-membered ring by the double bond, and to the presence of the methyl group adjacent to the double bond.

Bordwell, Suter, and Webber (*J. Amer. Chem. Soc.*, 1945, **67**, 827) concluded that the reaction between dioxan–sulphur trioxide complex and an olefin could be regarded as a nucleophilic replacement reaction :

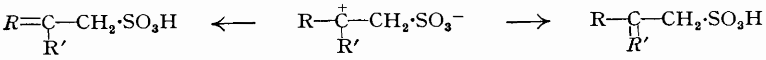


$$\mathrm{R{-}\underset{R'}{C}{=}CH_2} \rightleftarrows \mathrm{R{-}\underset{R'}{\overset{+}{C}}{-}\overset{-}{C}H_2} \longrightarrow \mathrm{R{-}\underset{R'}{\overset{+}{C}}{-}CH_2{\cdot}SO_3^-}$$

If R or R′ were hydrogen, the next step would be addition of a second molecule of sulphur trioxide to give an anhydro sulphated hydroxy-sulphonic acid which would yield a hydroxy-sulphonic acid on hydrolysis :



If, however, R or R′ were alkyl or phenyl, the predominant reaction after the initial reaction would be migration of a proton to give unsaturated sulphonic acids, the proton being released from one of the carbon atoms adjacent to that bearing the positive charge :



$$\mathit{R}\mathrm{{=}\underset{R'}{C}{-}CH_2{\cdot}SO_3H} \longleftarrow \mathrm{R{-}\underset{R'}{\overset{+}{C}}{-}CH_2{\cdot}SO_3^-} \longrightarrow \mathrm{R{-}\underset{\overset{\|}{\mathit{R}'}}{C}{-}CH_2{\cdot}SO_3H}$$

(*R* = R − H)

The behaviour of *cyclo*hexene differs from that predicted above in that it tends to behave in a manner similar to that of an olefin in which two alkyl groups are attached to one of the

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unsaturated carbon atoms, this being due probably to the increased activity of the α-methylenic hydrogen atom in *cyclo*hexene.

The production of 1-methyl*cyclo*pentene-5-sulphonic acid from 1-methyl*cyclo*pentene is in accordance with the predictions of Bordwell, Suter, and Webber, and lends support to their contention that the sulphonation of olefins is not brought about by substitution, which would have tended to result in the formation of 1-methyl*cyclo*pentene-3-sulphonic acid.

EXPERIMENTAL.

(M.p.s are corrected.)

cyclo*Hexene.*

Sulphonation of cyclo*Hexene.*—94·75 G. (1·15 mols.) of peroxide-free *cyclo*hexene were treated with 395 g. (2·3 mols.) of dioxan–sulphur trioxide in the presence of ethylene dichloride (400 ml.), the temperature being maintained at 0°. After 1 hour, the mixture was diluted with water, the ethylene dichloride layer removed, and the aqueous layer neutralised with barium hydroxide. The barium sulphate was removed by filtration, and the filtrate evaporated to small bulk under reduced pressure. The resulting barium salts were separated by fractional crystallisation from aqueous alcohol, and the following products separated in order of increasing solubility (total yields): *barium* cyclo*hexene*-3-*sulphonate*, 105·1 g.; *barium* 2-*sulpho*cyclo*hexyl hydrogen sulphate*, 55·4 g.; dimer derivatives, 30·8 g. In addition, 6·3 g. of a *cyclo*hexene(?-4-)sulphonate was obtained.

cyclo*Hexene*-3-*sulphonic acid*. The barium salt crystallised in hexagonal plates analysing as the monohydrate (Found: Ba, 28·69. $C_{12}H_{18}S_2O_6Ba,H_2O$ requires Ba, 28·76%). It became anhydrous on heating to 120°. The aqueous solution decolorised potassium permanganate solution and bromine water, only a trace of barium sulphate being precipitated by the latter reagent. Oxidation with alkaline potassium permanganate at 0° gave glutaric acid, m. p. and mixed m. p. 96—98° (Found: equiv., 65. Calc. for $C_5H_8O_4$: equiv., 66). The sulphonic acid gave a benzylthiuronium salt, needles, m. p. 150—151°, and a phenylhydrazine derivative, needles, m. p. 141—143°.

Anhydro- "trans"-2-*sulpho*cyclo*hexyl hydrogen sulphate*. This compound was not isolated as such, but as its hydrolysis product in the form of barium "*trans*"-2-sulpho*cyclo*hexyl hydrogen sulphate (Found: 30·4. $C_6H_{10}S_2O_7Ba,3H_2O$ requires Ba, 30·53%), which could be further hydrolysed by heating in water at 125° for 4 hours. The resulting barium "*trans*"-*cyclo*hexanol-2-sulphonate was isolated as hexagonal plates, readily soluble in water and aqueous alcohol. It was acetylated by heating under reflux with a mixture of equal parts of acetic acid and acetic anhydride for 2 hours and sulphated by treatment with oleum at 0°. Oxidation with nitric acid (*d*, 1·26) gave adipic acid, m. p. and mixed m. p. 150—151°, giving a benzylthiuronium salt as needles, m. p. 156—157°.

The properties of this *cyclo*hexanol-2-sulphonic acid differed from those of the acid synthesised either from *cyclo*hexene oxide or from 2-chloro*cyclo*hexanol. Since the properties of the latter, *viz.*, low solubility in water and inability to form a benzylthiuronium derivative, indicated hydrogen bonding, it was decided to call it the "*cis*"-compound as it was considered that the proximity of the hydrogen atom of the hydroxyl group to one of the co-ordinated oxygen atoms of the sulphonic acid group in the case of "*cis*"-isomer would facilitate hydrogen bonding.

Consideration of the configuration of the *cyclo*hexanol-2-sulphonic acid molecule by means of Fischer–Hirschfelder atomic models showed that with both the "chair" and the "boat" configuration of the *cyclo*hexane ring, the distances between the various "*trans*"-positions vary. The same applies to the "*cis*"-isomers. Treating each pair of carbon atoms in the *cyclo*hexane ring separately, hydrogen bonding would be possible in only six of the twelve possible forms of the "*trans*"-isomer with the "chair" configuration, and in four of the twelve forms with the "boat" configuration. With the "*cis*"-isomer, bonding is possible in all twenty-four positions. Hydrogen bonding is thus favoured in the case of the "*cis*"-isomer.

The properties of the two isomers are compared in the table below.

	Barium *cyclo*hexanol-2-sulphonates,	
	"*cis*"-isomer.	"*trans*"-isomer.
Crystal form	Hexagonal plates	Hexagonal plates
Solubility in water at 18°, g. per 100 g. of solution	8·22	17·75
Benzylthiuronium salt	Not formed	Needles, m. p. 156—157°
Phenylhydrazine derivative	Diamond-shaped plates, m. p. 140—141°	Diamond-shaped plates, m. p. 158—159°
	(mixed m. p. 128—132°)	

Each isomer gives a hydrogen sulphate on treatment with sulphuric acid or oleum, and an acetate on heating it under reflux with a 1 : 1 mixture of acetic acid and acetic anhydride. The hydrogen sulphate of the "*cis*"-isomer exhibits abnormally low solubility, whereas the solubility of the acetate appears to be normal.

"cis"-cyclo*Hexanol*-2-*sulphonic Acid.*—This acid has been prepared by the action of hydrogen sulphites on *cyclo*hexene oxide (cf. Lauer and Hill, *J. Amer. Chem. Soc.*, 1936, **58**, 1873; Brunel, *Bull. Soc. chim.*, 1903, [iii], **29**, 884). It can also be prepared by heating 2-chloro*cyclo*hexanol (20 g.) on a steam-bath for 3 days with ammonium sulphate (20 g.) in water (100 ml.). It was isolated as the barium salt (27·0 g., 73%).

Dimer Derivatives.—The barium salts (see above) consisted of approx. equal proportions of the sulphated hydroxy-sulphonic acid and the olefinic acid. They formed resin-like uncrystallisable salts, readily soluble in both water and alcohol.

In addition to the products described above, a small yield (6.3 g.) of an olefinic acid was obtained. The barium salt formed colourless diamond-shaped plates and gave a benzylthiuronium salt, m. p. and mixed m. p. with the salt of *cyclo*hexene-3-sulphonic acid, 146—147°. Oxidation with nitric acid (conc. acid 2, water 7 parts) at 100° gave succinic acid, but it was not possible to prove that it was actually *cyclo*hexene-3-sulphonic acid so that the possibility remains that it might have been *cyclo*hexene-4-sulphonic acid.

Synthesis of cyclo*Hexene-3-sulphonic Acid.*—3-Bromo*cyclo*hexene [prepared by the action of *N*-bromosuccinimide on *cyclo*hexene (Ziegler *et al.*, *Annalen*, 1942, **551**, 80)], b. p. 75—76°/30 mm., n_D^{20} 1·5142 (Found : Br, 49·1. Calc. for C_6H_9Br : Br, 49·7%) (10·65 g.) was heated on the steam-bath for 4 days with ammonium sulphite (7·7 g.) in water 40 ml., air being excluded by means of nitrogen or carbon dioxide. The product was treated with barium hydroxide, and barium *cyclo*hexene-3-sulphonate was obtained as colourless hexagonal crystals (Found : Ba, 28·65%) (1·2 g.), having the same properties and giving the same derivatives (mixed m. p.) as the salt described above.

1-*Methyl*cyclo*pentene.*

Preparation.—*cyclo*Pentanone was prepared from adipic acid and barium hydroxide (Thorpe and Kon, *Org. Synth.*, Coll. Vol. I) and then treated with methylmagnesium iodide according to Zelinsky and Nametkin (*Ber.*, 1902, **35**, 2683). The product was treated with water and the resulting 1-methyl*cyclo*pentanol dehydrated to 1-methyl*cyclo*pentene by distilling it over anhydrous potassium carbonate. The product was purified by fractionation and then had b. p. 75·5°/752 mm., d_4^{20} 0·7758, n_D^{20} 1·4352, bromine no. 193. It was oxidised by alkaline potassium permanganate at 0° to pentan-4-one-1-carboxylic acid hydrate, m. p. 35—37° (Block and Thomas, *J. Amer. Chem. Soc.*, 1944, **66**, 1589, give m. p. 36—37°).

Sulphonation.—A suspension of dioxan–sulphur trioxide complex in ethylene dichloride was prepared containing 37 g. of sulphur trioxide. To the well stirred mixture, cooled to 0°, a solution of 19·68 g. of 1-methyl*cyclo*pentene in ethylene dichloride was gradually added. Unlike the reaction with *cyclo*hexene, the mixture did not thicken but became clear and fluid after the completion of the reaction (½ hr.). The mixture was then diluted with water, the ethylene dichloride layer separated, the aqueous layer neutralised with barium hydroxide, and the precipitated barium sulphate filtered off. The filtrate was evaporated to small bulk under reduced pressure, and alcohol was added to precipitate the *disulphonates*, which were purified by reprecipitation and gave 13·5 g. of dried material (*A*) (see below). The alcoholic filtrate was evaporated to small bulk under reduced pressure and allowed to crystallise. 37·7 G. of crystals were obtained, which consisted of *barium* 1-*methyl*cyclo*pentene*-5-*sulphonate*. No sulphated hydroxy-sulphonic acids were present.

The above barium salt crystallises from aqueous alcohol in needles [Found : Ba, 27·63. $(C_6H_9SO_3)_2Ba,2H_2O$ requires Ba, 27·68%]. It loses one molecule of water at 120° but decomposes when heated to 140°. It is readily soluble in water or 90% alcohol, and is not precipitated on addition of excess of alcohol. With alkaline potassium permanganate at 0° it gives succinic acid, m. p. and mixed m. p. 183—184° (Found : equiv., 61·4. Calc. for $C_4H_6O_4$: equiv., 59), and acetic acid (benzylthiuronium salt, elongated rectangular plates, m. p. and mixed m. p. 134—136°) which establishes the constitution of the acid. The aqueous solution of the barium salt readily decolorises bromine water, but no barium sulphate is precipitated.

The benzylthiuronium salt crystallised from 50% aqueous alcohol in needles, m. p. 79—80·5°. The phenylhydrazine derivative was unobtainable owing to decomposition of the acid on the steam-bath.

Action of Sulphuric Acid.—This reaction is of particular interest in that it demonstrates the weakness of the carbon–sulphur bond in 1-methyl*cyclo*pentene-5-sulphonic acid. The dry barium salt of this acid was added slowly to concentrated sulphuric acid at room temperature. A vigorous reaction ensued with evolution of heat and sulphur dioxide. On pouring the mixture into water, a green oil separated which appeared to consist of a mixture of unsaturated polymers.

Barium Disulphonates Insoluble in 75% *Alcohol.*—The yellow solid (*A*, above) could not be crystallised (Found : Ba, 34·3. $C_6H_8S_2O_6Ba,H_2O$ requires Ba, 34·7%).

Summary of Yields.—The following are total yields, based on the hydrocarbon. (*a*) Barium *cyclo*hexenesulphonate, 40·5; barium "*trans*"-2-sulpho*cyclo*hexyl hydrogen sulphate, 55·4; dimers, 17·3; total, 68·4%. (*b*) Barium 1-methyl*cyclo*pentene-5-sulphonate, 63·4; barium methyl*cyclo*pentenedisulphonates, 14·1; total, 77·5%.

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