in mμ: 258 (ϵ 17,200), 310 (ϵ 9, 150); $\lambda_{\max}^{CCl_4}$ in μ 4.12 (moderately strong, intramolecularly hydrogen bonded SH), 5.75 (hook, COOEt of thione tautomer), 5.95 (strong, intramolecularly hydrogen bonded α,β-unsaturated COOEt).

Another sample was purified by precipitation with lead acetate and regeneration with hydrogen sulfide as described for the *p*-ethoxy compound. The same m.p. and infrared spectrum were obtained.

Anal. Calcd. for $C_{11}H_{11}NO_4S$: C, 52.2; H, 4.38; S, 12.65; mol. wt., 253. Found: C, 52.3; H, 4.48; S, 12.44; mol. wt., 246 (cryoscopic).

Diethyl β,β'-Dithiobis-(*p*-nitrocinnamate).—A solution of 0.0236 g. (0.00093 mole) of iodine in 2 ml. of 95% ethanol was added dropwise at room temperature to a swirled solution of 0.047 g. (0.00186 mole) of ethyl *p*-nitrothiobenzoylacetate in 3 ml. of 95% ethanol. The iodine color was discharged almost immediately following the addition of each drop, and a white precipitate settled out during the course of the addition. The mixture was allowed to stand for two hours at room temperature, cooled and filtered. The precipitate was washed with and twice recrystallized from, 95% ethanol, and twice recrystallized from a mixture of benzene and petroleum ether (30–65°). The cream-colored product (0.033 g., 35% yield) melted at 153–154°; spectral data $\lambda_{\max}^{chloroform}$ in μ: 5.84 with shoulder at 5.90 (strong, α,β-unsaturated COOEt).

Anal. Calcd. for $C_{22}H_{20}N_2O_9S_2$: S, 12.6. Found: S, 12.3.

Oxidation of Ethyl *p*-Nitrothiobenzoylacetate.—A solution of 0.20 g. (0.00079 mole) of ethyl *p*-nitrothiobenzoylacetate in 25 ml. of 95% ethanol was saturated with dried oxygen, stoppered and allowed to stand at room temperature. Cream-colored crystals gradually separated from the solution over a period of three days. The crystalline product was filtered, washed with alcohol, and with carbon tetrachloride, and crystallized from benzene; yield 0.029 g. (46%), m.p. 154–155°. The infrared spectrum in chloroform was identical with that of diethyl β,β'-dithiobis-(*p*-nitrocinnamate).

Anal. Calcd. for $C_{22}H_{20}N_2O_8S_2$: S, 12.6; mol. wt., 504.5. Found: S, 12.4; mol. wt. (isothermal distillation in benzene), 518.

MENLO PARK, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Elimination Reactions. IX. Mechanisms for the Pyrolysis of Methyl Cyclohexyl Sulfites

BY F. G. BORDWELL AND PHILLIP S. LANDIS[1]

RECEIVED MAY 26, 1958

The pyrolyses of *cis*- and *trans*-2-*p*-$C_7H_7SO_2$-, *cis*- and *trans*-2-*p*-C_7H_7S- and *cis*-2-*t*-butyl-cyclohexyl methyl sulfites were found, for the most part, to parallel those of the corresponding S-methyl xanthates (*i.e.*, *cis* elimination). Evidence is presented to show that the formation of considerable quantities of 1-substituted-cyclohexene (the *trans* elimination product) from *cis*-2-C_7H_7S- and *cis*-2-C_6H_5-cyclohexyl methyl sulfites is caused largely by rearrangement of the 3-substituted-cyclohexene first formed, rather than by a *trans* elimination. It is concluded that methyl cyclohexyl sulfite pyrolyses probably occur by the concerted type mechanism generally accepted for xanthate and other ester pyrolyses. An ion pair mechanism *without participation* is an acceptable variation. Decomposition of *cis*-2-*p*-tolylsulfonylcyclohexyl methyl sulfite occurs by a *trans* elimination following first-order kinetics. This is represented by a stepwise reaction involving a dipolar intermediate.

Recently it was observed that pyrolysis of *cis*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate gave 1-*p*-tolylsulfonylcyclohexene.[2] This is apparently the first example in which a Chugaev elimination proceeds by abstraction of a *trans* β-hydrogen *in preference* to a *cis* β-hydrogen. Our attention was attracted in this respect to the conclusion by Berti[3] that the pyrolysis of *cis*-2-phenylcyclohexyl methyl sulfite to give 1-phenylcyclohexene (78%) in preference to 3-phenylcyclohexene (22%) was an example of a *trans* pyrolytic elimination. Since this result was opposite to that obtained on pyrolysis of the S-methyl xanthate,[3,4] Berti concluded that sulfite and xanthate pyrolyses proceed by different mechanisms, and Berti and Price[5] suggested an ion pair mechanism with group participation for sulfite pyrolyses. Our study of xanthate pyrolyses[2] now has been extended to methyl sulfites.

Pyrolysis of the methyl sulfite of *cis*-2-*p*-tolylsulfonylcyclohexyl methyl sulfite gave 1-*p*-tolylsulfonylcyclohexene, the *trans* elimination product, and no detectable quantity of 3-*p*-tolylsulfonylcyclohexene. This parallels the result with the corresponding xanthate.[2] Pyrolysis of *cis*-2-*p*-tolylthiocyclohexyl methyl sulfite gave about 40% of the *trans* elimination product (1-*p*-tolylthiocyclohexene) and 60% of the *cis* elimination product (3-*p*-tolylthiocyclohexene). Before concluding that 1-substituted-cyclohexenes are formed from *cis*-esters by *trans* eliminations it is necessary to show that rearrangement of the 3-substituted-cyclohexene to 1-substituted-cyclohexene does not occur during the pyrolysis. The fact that 3-*p*-tolylsulfonylcyclohexene fails to rearrange in the presence of strong acid[2] ensures that a *trans* elimination is indeed occurring with the sulfite (and xanthate) pyrolysis when the *cis* 2-substituent is *p*-$C_7H_7SO_2$. In contrast, 3-*p*-tolylthiocyclohexene rearranges to 1-*p*-tolylthiocyclohexene to the extent of 40% in 20 min. at 195° in the presence of *p*-toluenesulfonic acid. When added to a sulfite pyrolysis 3-*p*-tolylthiocyclohexene rearranges to 1-*p*-tolylthiocyclohexene to the extent of about 20%. This suggests that in the pyrolysis of *cis*-2-*p*-tolylthiocyclohexyl methyl sulfite a maximum of 20% (40–20) of *trans* elimination occurred. Berti[3] found that 3-phenylcyclohexene rearranged to 1-phenylcyclohexene to the extent of about 35% under pyrolysis conditions. Actually, these are probably minimum figures for rearrangement, since in the test cases the added olefin is present in high concentration relative to the acidic products causing rearrangement, whereas the olefin formed *in*

---

[1] Socony-Mobil Predoctoral Fellow, 1955–1958.

[2] F. G. Bordwell and P. S. Landis, THIS JOURNAL, **80**, 2450 (1958).

[3] G. Berti, *ibid.*, **76**, 1213 (1954).

[4] E. R. Alexander and A. Mudrak, *ibid.*, **73**, 59 (1951).

[5] See footnote 25 of reference 3.

situ probably is not. On the basis of more recent evidence Berti's value of 78% for the amount of *trans* elimination product has been corrected to 57%.[6] Using this value the maximum amount of *trans* elimination is probably 22% (57–35), as compared to at least 43% of *cis* elimination. The authors[6] still favor an ion pair mechanism, but appear to have abandoned the idea of participation.

Since the results with *cis*-2-phenyl- and *cis*-2-*p*-tolylthiocyclohexyl methyl sulfites are somewhat indecisive because of the sensitivity to rearrangement of the product formed by *cis* elimination, the study was extended to *cis*-2-*t*-butylcyclohexyl methyl sulfite. This provides a good case to test *cis vs. trans* elimination since both of the possible olefinic products, 3-*t*-butylcyclohexene and 1-*t*-butylcyclohexene, have been shown to be essentially unchanged after heating with 85% phosphoric acid at 130–150° for 7.5 hr.[7]

Pyrolysis of *cis*-2-*t*-butylcyclohexyl methyl sulfite gave 3-*t*-butylcyclohexene containing less than 5% of 1-*t*-butylcyclohexene. Similar results were obtained by pyrolysis of *cis*-2-*t*-butylcyclohexyl S-methyl xanthate. A comparison of the products obtained from various cyclohexyl methyl sulfite and xanthate pyrolyses is given in Table I. The product analyses in the present work were made by comparing the spectra of the pyrolysis products with those of standards consisting of known mixtures of the 1- and 3-substituted olefins.

TABLE I

PRODUCTS FROM THE PYROLYSIS OF METHYL *cis*- AND *trans*-2-SUBSTITUTED-CYCLOHEXYL SULFITES AND XANTHATES

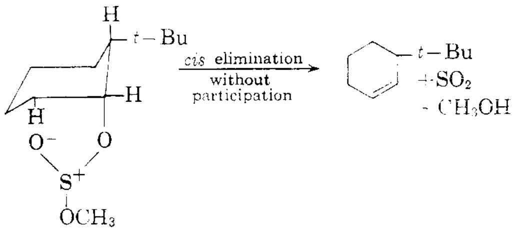
2-Substituent	Methyl sulfite or S-methyl xanthate	1-Substituted cyclohexene, %	3-Substituted cyclohexene, %	Predominant elimination
cis-*i*-Pr[a]	Sulfite[3]	35	65	*cis*
cis-*i*-Pr[a]	Xanthate[b]	30	70	*cis*
cis-*t*-Bu	Sulfite	5	95	*cis*
cis-*t*-Bu	Xanthate	0	100	*cis*
cis-$C_7H_7SO_2$	Sulfite	100	0	*trans*
cis-$C_7H_7SO_2$	Xanthate[2]	90	10	*trans*
cis-C_7H_7S	Sulfite	40	60	*cis*
cis·C_7H_7S	Xanthate	10	90	*cis*
cis-C_6H_5	Sulfite[3]	57[6](78[3])	43[6](22[3])	*cis*[c]
cis-C_6H_5	Xanthate[4]	4	96	*cis*
trans-$C_7H_7SO_2$	Sulfite	100	0	*cis*
trans-$C_7H_7SO_2$	Xanthate[2]	90	10	*cis*
trans-C_7H_7S	Sulfite	80	20	*cis*
trans-C_7H_7S	Xanthate	90	10	*cis*
trans-C_6H_5	Sulfite[3]		[d]	
trans-C_6H_5	Xanthate[4]	88	12	*cis*

[a] Methyl sulfite or xanthate of *l*-menthol. [b] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940). [c] When rearrangement is taken into account (see text). [d] Twenty-one per cent. of rearranged product reducible to benzylcyclopentane is formed.[6]

It seems clear from the results in Table I that pyrolyses of methyl sulfites and xanthates generally give similar results. The exceptions are instances where the olefins formed are sensitive to acid-catalyzed rearrangement, and, as pointed out by Berti,[3] acidic products are more likely to be formed in sulfite than in xanthate pyrolyses.

The original suggestion of an ion pair mechanism with participation in methyl sulfite pyrolyses to give olefins[3,5] was made (1) on the basis of analogy with ion pair formation in pyrolyses which give ethers,[8a] (2) to explain the formation of rearranged products in some pyrolyses,[8b] and (3) to explain the predominant *trans* elimination then believed to occur in the pyrolysis of *cis*-2-phenylcyclohexyl methyl sulfite.[3] The latter basis has been removed by the correction of the earlier results[6] and our further demonstration of olefin isomerizations during methyl sulfite pyrolyses. However, an ion pair mechanism remains as an attractive alternative for (or variation of) the quasi six-membered ring transition state, which generally has been accepted[9] for ester pyrolyses.

The pyrolysis of *cis*-2-*t*-butylcyclohexyl methyl sulfite would appear to offer an optimum opportunity for an ion pair mechanism with hydrogen participation.[10] The hydrogen alpha to the *t*-butyl group is held in the axial position desirable for participation and inductive electron release from the *t*-butyl group is favorable to the formation of a hydrogen bridged cation and consequent *trans* elimination (according to the original ion pair mechanism.)[3] The fact that pyrolysis gives at least 95% *cis* elimination is unfavorable to this interpretation. This result is in agreement with the failure of Goering and Reeves to find evidence for hydrogen participation in the solvolysis of *cis*-2-*t*-butylcyclohexyl *p*-toluenesulfonate.[11] The *cis* elimination is, of course, consistent with the quasi six-membered ring type transition state usually written for ester pyrolyses.[9] It is also possible to account for preferential *cis* elimination by assuming that ion pair formation *without participation* occurs and that the anion abstracts the nearest proton.[6] For most ester pyrolyses such an ion pair is, no doubt, merely a contributing resonance form of the quasi six-membered transition state. However, in some systems it may acquire a reality of its own. For example, the partial rearrangement observed on pyrolysis of *trans*-2-phenylcyclohexyl methyl sulfite[6] and the *trans* eliminations to form 2-methylindene occurring on pyrolysis of *cis*-2-methyl-1-indanyl xanthate and acetate[12] are better accommodated by the latter mechanism.



---

[6] E. L. Eliel, J. W. McCoy and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957).

[7] H. L. Goering, R. L. Reeves and H. H. Espy, THIS JOURNAL, **75**, 4926 (1956).

[8] (a) C. C. Price and G. Berti, *ibid.*, **76**, 1207 (1954); (b) C. C. Price and G. Berti, *ibid.*, **76**, 1211 (1954).

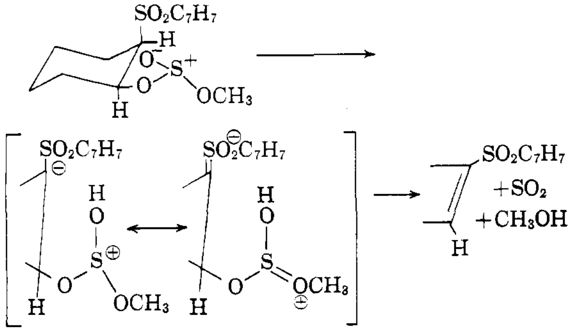
[9] See the discussion by D. J. Cram in Chapter 6 of "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Son, Inc., New York, N. Y., 1956.

[10] S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

[11] H. L. Goering and R. L. Reeves, *ibid.*, **78**, 4931 (1956).

[12] E. R. Alexander and A. Mudrak, *ibid.*, **73**, 59 (1951).

The *trans* elimination of $HOSO_2CH_3$ [SO_2 + CH_3OH] from *cis*-2-*p*-tolylsulfonylcyclohexyl methyl sulfite is believed to occur by way of a dipolar ion intermediate similar to that used to explain *trans* elimination from the corresponding xanthate.[2] Like the xanthate[2] the decomposition followed a first-order rate law, which shows that the reaction is intramolecular.



Pyrolysis of *trans*-2-*p*-tolylsulfonylcyclohexyl methyl sulfite gave 1-*p*-tolylsulfonylcyclohexene at a rate about three times that by which this product was formed from the *cis* isomer. This *cis* elimination may be concerted, but in view of the similarity in the rates it seems preferable to represent it by a dipolar ion intermediate comparable to that shown for the *trans* elimination. The transition state for the *cis* elimination would be expected to have a lower energy, since the large $C_7H_7SO_2$ group occupies an equatorial rather than an axial position, and the faster rate for the *cis* elimination can be rationalized on this basis. A similar situation exists for the corresponding xanthate pyrolyses.[13]

An ion pair mechanism *involving hydrogen participation* is unlikely for these *trans* eliminations since the *p*-$C_7H_7SO_2$ group would strongly inhibit a process by which the α-hydrogen was required to donate electrons. Ion pair formation without participation would also be inhibited by the $C_7H_7SO_2$ group. The fact that the rate of pyrolysis is accelerated by the presence of the $C_7H_7SO_2$ group (Table II) would require that if the ion pair mechanism[6] is to be used it must be assumed that the rate of abstraction of the proton by the anion, rather than formation of the ion pair, is rate determining.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE PYROLYSIS OF METHYL *cis*- AND *trans*-2-*p*-TOLYLSULFONYLCYCLOHEXYL SULFITES AND XANTHATES

Compound	Type of elimination	k_1, sec.$^{-1}$	T, °C.
trans-Sulfite	*cis*	1.4×10^{-4}	150 ± 1
cis-Sulfite	*trans*	0.48×10^{-4}	150 ± 1
trans-Xanthate	*cis*	1.7×10^{-4}	166 ± 1
cis-Xanthate	*trans*	0.73×10^{-4}	166 ± 2
Cholesteryl xanthate[14]	*cis*	0.05×10^{-4}	166

Table II compares the sulfite and xanthate rate data and shows a value for cholesteryl S-methyl xanthate extrapolated from the data of O'Connor and Nace.[14] At comparable temperatures the rates of decomposition of the sulfites would probably be about twice those of the corresponding xanthates. This contrasts with Berti's observation that methyl sulfites usually have higher decomposition points than do S-methyl xanthates.[3] However, the pyrolyses of 2-*p*-tolylsulfonylcyclohexyl sulfites and xanthates probably occur by way of a dipolar ion intermediate, whereas the other pyrolyses are concerted. The positive charge in the sulfite dipolar intermediate is on sulfur and that in the xanthate dipolar ion is on carbon. The greater stability of a sulfonium *vs.* carbonium intermediate may thus be invoked to account for the apparent reversal in relative ease of methyl sulfite *vs.* xanthate pyrolyses.

The activation of a cyclohexyl xanthate pyrolysis by substitution of *p*-$C_7H_7SO_2$ for H is seen from Table II to lead to about a 35-fold increase in rate (comparing the *trans*-xanthate and cholesteryl xanthate). The *p*-$C_7H_7SO_2$ group increases the rate of E2 type reaction by factors of 10^6–10^9.[15] This startling difference in activating effect contrasts the ability of a reaction in solution to take advantage of a change to a more ionic type transition state to the inability of a reaction not having large solvation forces at its disposal to profit by a similar change.

Experimental[16]

Methyl *trans*-2-*p*-Tolylsulfonylcyclohexyl Sulfite.—*trans*-2-*p*-Tolylsulfonylcyclohexanol[17] (3.8 g., 0.015 mole) and 1.4 g. (0.0177 mole) of dry pyridine were dissolved in 20 ml. of dry ether, and the solution cooled to 0° in an ice–salt-bath. A cold solution of 2.0 g. (0.0175 mole) of methyl chlorosulfinate in 10 ml. of dry ether was added with stirring, and the mixture was stirred for an additional hour at 0°. The precipitated pyridinium chloride was removed by filtration and the ether solution was washed successively with water, 5% hydrochloric acid and 5% sodium hydroxide. The ether extract was dried over anhydrous sodium sulfate, filtered and the solvent removed at room temperature. The residue, 4.1 g. (82%), crystallized on standing. Recrystallization from hexane gave a solid melting at 82–84°.

Anal. Calcd. for $C_{14}H_{20}O_5S_2$: C, 50.58; H, 6.06. Found: C, 50.69; H, 6.00.

Methyl *cis*-2-*p*-Tolylsulfonylcyclohexyl Sulfite.—*cis*-2-*p*-Tolylsulfonylcyclohexanol[18] (1.1 g., 0.0044 mole) and 0.4 g. (0.0054 mole) of dry pyridine were dissolved in 10 ml. of dry dioxane, and 0.575 g. (0.0050 mole) of methyl chlorosulfinate was added while the solution was kept at 5°. Processing as described above gave 1.25 g. (85%) of crystalline material, m.p. 106–108°. Recrystallization from benzene–hexane failed to raise the melting point.

Anal. Calcd. for $C_{14}H_{20}O_5S_2$: C, 50.58; H, 6.06. Found: C, 50.94; H, 5.98.

Pyrolysis of Sulfone Sulfites.—Samples were placed in erlenmeyer flasks contained in a heated oil-bath (200°) for about 1 hr. A slow stream of nitrogen was passed over the surface of the decomposition liquid during this time to sweep out sulfur dioxide and methanol. The resulting crude residues were recrystallized once from hexane. Analyses of

---

[13] A Referee has criticized the dipolar intermediate mechanism on the grounds that from the work of E. L. Eliel and R. S. Ro, THIS JOURNAL, **79**, 5995 (1957), the *cis* sulfone must be almost entirely in the conformation where the $C_7H_7SO_2$ group is equatorial and the OSO_2CH_3 group axial. However, pyrolyses of this type have large activation energies[14] and the geometry of the transition state may differ markedly from that of the ground state. Therefore, we do not feel that the fact that relatively few molecules of this conformation are present in the ground state rules out the possibility that this is a favorable transition state for the production of the dipolar ion shown.

[14] G. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5454 (1952).

[15] See H. L. Goering, D. I. Relyea and K. L. Howe, *ibid.*, **79**, 2502 (1957).

[16] Microanalyses were by Miss Hilda Beck.

[17] F. G. Bordwell and R. J. Kern, THIS JOURNAL, **77**, 1145 (1955).

[18] J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3468 (1956).

ethanol solutions of the products were made using a Beckman DK-2 recording spectrophotometer. Concentrations of 4×10^{-5} *M* in 95% ethanol gave about 60% transmittance. The composition of the product was determined by the position of the absorption maximum using 1-*p*-tolylsulfonyl-1-cyclohexene (λ_{max} 235 mμ) and 3-*p*-tolylsulfonyl-1-cyclohexene (λ_{max} 226 mμ) as standards.[2] The total yield of olefin was about 90%, which was in each instance essentially pure 1-*p*-tolylsulfonyl-1-cyclohexene.

For the kinetic runs a series of small samples were pyrolyzed as described above in tared erlenmeyers contained in a bath kept at 150 ± 1°. The flasks were removed and weighed at convenient intervals. Plots of log "% unreacted" against time gave surprisingly good straight lines, considering the crudity of the method. The rate constants were determined from the slope of the lines, $k_1 = -\text{slope}/2.303$. This is essentially the procedure of O'Connor and Nace.[14] A typical kinetic run is given in Table III.

TABLE III

KINETIC DATA FOR THE PYROLYSIS OF METHYL *cis*-2-*p*-TOLYLSULFONYL SULFITE AT 150 ± 1°

Time, sec.	Wt. loss, g.	Reacted, %	Unreacted, %	Log % unreacted
0	0	0	100	2.000
166	0.0006	1.5	98.5	1.993
432	.0016	3.9	96.1	1.983
724	.0022	5.2	94.8	1.977
1149	.0025	6.1	93.9	1.972
1713	.0034	8.3	91.7	1.963
4400	.0081	19.6	80.4	1.905
7150	.0122	29.7	70.3	1.847
12493	.0189	45.6	54.4	1.736

Preparation and Pyrolysis of Methyl *cis*- and *trans*-2-*p*-Tolylthiocyclohexyl Sulfites.—The procedure described above for the preparation of the sulfites when applied to *cis*- and *trans*-2-*p*-tolylthiocyclohexanols[2] gave viscous oils which resisted all attempts at crystallization. These were pyrolyzed directly in a 25-ml. distillation flask fitted with a 3-inch Vigreux head. The sulfite was heated to 200° under nitrogen at atmospheric pressure for about 30 min. Vacuum (1 mm.) then was applied and the decomposition products were distilled slowly from the reaction mixture. The olefins were condensed in the air-cooled receiver and the methanol and sulfur dioxide allowed to pass into the Dry Ice trap. The yield of olefin was 86% from the *cis* isomer and 76% from the *trans*. Analysis for the percentage of 1-substituted and 3-substituted cyclohexene was made by oxidation to the sulfones and determination of the position of the absorption maximum in the ultraviolet spectra (see above and ref. 2). The oxidized product from the *cis* isomer had an absorption maximum at 229 mμ corresponding to that of a mixture of 40% 1-*p*-tolylsulfonyl-1-cyclohexene and 60% of 3-*p*-tolylsulfonyl-1-cyclohexene. The oxidized product from the *trans* isomer had its absorption maximum at 232 mμ, corresponding to 80% of the 1-substituted isomer.

Isomerization of 3-*p*-Tolylthio-1-cyclohexene During Pyrolysis.—Four grams (0.013 mole) of methyl *trans*-2-*p*-tolylthiocyclohexyl sulfite and 2.65 g. (0.013 mole) of 3-*p*-tolylthio-1-cyclohexene were placed in a small vacuum distillation flask fitted with a 3-inch Vigreux head. The mixture was heated under nitrogen for 20 min. at 190° at atmospheric pressure and then vacuum was applied slowly until the pressure was about 1 mm. Volatile products slowly were removed in the course of about 2 hr. The primary distillate, 4.4 g., distilled at 135-140° (1.1 mm.). A portion of this distillate was oxidized with hydrogen peroxide in acetic acid and the gummy solid, m.p. 50-75°, was dissolved in 95% ethanol and the spectrum measured. The maximum at 230 mμ indicated a mixture of 70% 1-*p*-tolylsulfonyl-1-cyclohexene. If no rearrangement had occurred the mixture should have contained 40 and 60% of 1- and 3-isomers, respectively (the percentages are 20% and 80% from methyl *trans*-2-*p*-tolylthiocyclohexyl sulfite). Therefore, rearrangement occurred to the extent of about 30%.

Acid-catalyzed Isomerization of 3-*p*-Tolylthio-1-cyclohexene.—To 100 mg. (0.00049 mole) of 3-*p*-tolylthio-1-cyclohexene was added 80 mg. (0.00043 mole) of *p*-toluenesulfonic acid monohydrate and 10 ml. of 1-octanol. The solution was refluxed for 20 min. at 195°. The solution was poured into water and extracted with chloroform. The chloroform extract was washed four times with 10-ml. portions of water, dried over anhydrous Na_2SO_4 and the solvent removed on a steam-bath. The crude residue (2 g.) containing some octanol was dissolved in 10 ml. of acetic acid and treated with 3 ml. of 30% hydrogen peroxide at 60-80° for two hours. After standing overnight the solution was poured into ice-water, the solid which separated was removed by filtration and the ultraviolet spectrum determined in 95% ethanol. The ultraviolet maximum was 229 mμ corresponding to about 40% 1-*p*-tolylsulfonyl-1-cyclohexene and 60% 3-*p*-tolylsulfonyl-1-cyclohexene.

Preparation and Pyrolysis of *cis*-2-*t*-Butylcyclohexyl S-Methyl Xanthate.—Small pieces of sodium (11.5 g., 0.5 g. atom) were added to a solution of 78 g. of *cis*-2-*t*-butylcyclohexanol[19] in 400 ml. of benzene. Reasonably rapid reaction occurred and at the end of four hours all but a trace of sodium had reacted leaving a thick gel. The gel was diluted with 400 ml. of benzene, stirred briefly, and 40 g. of carbon disulfide added. The solution was stirred and refluxed for eight hours after which methyl iodide (75 g.) was added and the solution refluxed overnight. The precipitated sodium iodide was removed by filtration (slowed by clogging of the filter pores by gel) and the solvent evaporated on a steam-bath leaving 91 g. of yellow solid, m.p. 41-43°.

Anal. Calcd. for $C_{12}H_{22}OS_2$: C, 58.48; H, 8.99. Found: C, 58.21; H, 9.11.

Twenty-four and six-tenths grams (0.1 mole) of xanthate was heated under light reflux at 200-205° for three hours, methanethiol and carbon oxysulfide swept out of the reaction solution using a slow stream of nitrogen gas. The yellow, oily residue was distilled at atmospheric pressure collecting 8.2 g. (60%) of 3-*t*-butyl-1-cyclohexene, b.p. 165-170°, $n^{25}\text{D}$ 1.4568. The product was established as exclusively 3-*t*-butylcyclohexene by comparison with infrared spectra kindly furnished by Prof. H. L. Goering.[7] The 11.90 μ peak, which is characteristic of 1-*t*-butylcyclohexene, was absent.

Preparation and Pyrolysis of Methyl *cis*-2-*t*-Butylcyclohexyl Sulfite.—A solution of 4.0 g. (0.051 mole) of anhydrous pyridine and 7.8 g. (0.05 mole) of purified[7] *cis*-2-*t*-butylcyclohexanol[16] in 70 ml. of dry ether was cooled to 0° in an ice-salt-bath. With rapid stirring 5.7 g. (0.05 mole) of methyl chlorosulfinate in 30 ml. of ether was added dropwise in 20 minutes. The solution was stirred for an additional 30 minutes and the precipitated pyridinium chloride separated by filtration. The ether solution was washed successively with 20-ml. portions of 5% sodium carbonate, 5% hydrochloric acid and water, dried over anhydrous sodium sulfate and the solvent removed at room temperature under a slow stream of nitrogen. The crude residue (10.2 g.) was distilled under vacuum using a 4-inch Vigreux column. There was obtained, after a small forerun of unreacted alcohol, 4.1 g. (35%) of water-white oil, b.p. 88-89° at 0.5 mm., $n^{25}\text{D}$ 1.4702.

Anal. Calcd. for $C_{11}H_{22}O_3S$: C, 56.37; H, 9.46. Found: C, 56.52; H, 9.52.

Four grams of methyl sulfite was placed in a distillation flask fitted with a 3-inch Vigreux. A slow stream of nitrogen was passed over the flask contents which were heated at 195-210° for two hours in an oil-bath. The pot temperature then was raised to 215-230° and distillate, 1.5 g. (64%), b.p. 170-178°, was collected. Infrared analysis of the olefin distillate indicated it to be at least 95% 3-*t*-butyl-1-cyclohexene with a maximum of 5% 1-*t*-butyl-1-cyclohexene.

EVANSTON, ILL.

---

[19] A sample kindly furnished by the Dow Chemical Co., Midland, Mich. It was specified as containing 84% of *cis*- and 16% *trans*-2-*t*-butylcyclohexanol.