[Contribution from the Chemistry Department of Northwestern University]

Elimination Reactions. VIII. A *trans* Chugaev Elimination[1]

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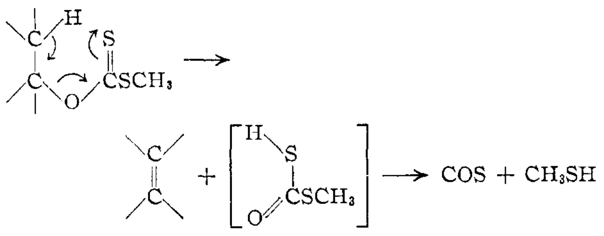
Pyrolysis of *cis*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate (II) gave almost exclusively 1-*p*-tolylsulfonyl-1-cyclohexene (III) (*trans* elimination) rather than the expected 3-*p*-tolylsulfonyl-1-cyclohexene (*cis* elimination). This is interpreted mechanistically as a *stepwise intramolecular trans elimination of equatorial groups promoted by the high acidity of the β-hydrogen being eliminated.* Pyrolysis of *trans*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate also gave III (*cis* elimination). The sulfide xanthate corresponding to II, *cis*-2-*p*-tolylthiocyclohexyl S-methyl xanthate, gave 3-*p*-tolylthio-1-cyclohexene on pyrolysis, which is the product expected (*cis* elimination). Pyrolysis of *trans*-2-*p*-tolylthiocyclohexyl S-methyl xanthate gave 1-*p*-tolylthio-1-cyclohexene (*cis* elimination).

As the result of a number of investigations[3-5] it is clear that the Chugaev pyrolysis of xanthates usually proceeds predominantly with the elimination of the xanthate grouping and a *cis*-β-hydrogen. It is generally agreed that the reaction occurs by way of a concerted mechanism in which the β-hydrogen atom is forming a bond with sulfur in a cyclic planar transition state at the same time that the α-carbon–oxygen bond is being broken.[3,4,6-9] The demonstration of first-order kinetics for the reaction[8] supports its representation as an intramolecular cyclic process. The pyrolyses of acetates, benzoates, carbonates and analogous esters are believed to occur by closely similar mechanisms.[4,5,8-10]

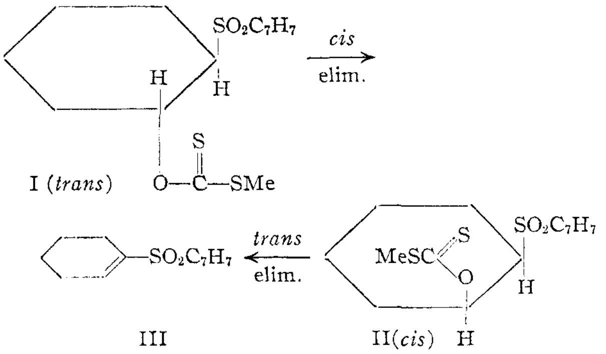


Although *cis* elimination is as a rule preferred, there is nevertheless evidence in the literature that ester pyrolyses can occur to some extent by *trans* eliminations. The following appear to be examples of *trans* eliminations: (1) the formation of 20% of 3-menthene by pyrolysis of the xanthate of neomenthol,[3] (2) the formation of 2-methylindene by pyrolysis of the xanthate or acetate of *cis*-2-methylindanol,[5b] and (3) the formation of a bridgehead olefin by pyrolysis of the α-decalol, m.p. 49°, of *trans*-decalin (the α-OH is *trans* to the bridgehead hydrogen).[3]

In previous work it has been shown that in cyclic systems *cis* E2 eliminations involving an acidic β-hydrogen may be preferred to *trans* elimination involving a non-activated β-hydrogen.[11] It seemed possible that the Chugaev reaction might also proceed in an unusual fashion in such systems, a *trans* elimination with an activated β-hydrogen taking precedence over a *cis* elimination with a non-activated β-hydrogen. This indeed appears to be the case.

The S-methyl xanthates of *trans*- and *cis*-2-*p*-tolylsulfonylcyclohexanol[11c] were prepared by successive treatment of the alcohols with potassium metal, carbon disulfide and methyl iodide in the usual manner, but the xanthates were non-crystalline and resisted attempts at purification. It was established, however, that at least 80% of xanthate had been formed, in each instance, by isolation of about this quantity of methanethiol on pyrolysis. The xanthates were shown to be different, since rough kinetic measurements indicated that the *trans*-xanthate I decomposed about twice as rapidly as did the *cis*-xanthate II.

Pyrolysis of both I and II gave the same product, 1-*p*-tolylsulfonyl-1-cyclohexene (III), although the yield was somewhat lower from II. This product can be formed from I by the usual elimination of *cis* groupings,[3-9] but the transformation II → III involves an elimination of *trans* groupings.



I (*trans*) III II(*cis*)

Since this is, to our knowledge, the first instance reported wherein a Chugaev reaction proceeds by a *trans* elimination *in preference* to a possible *cis* elimination (II could have given the β,γ-unsaturated sulfone, 3-*p*-tolylsulfonyl-1-cyclohexene (IV), rather than the α,β-unsaturated sulfone III), and since we did not use pure xanthates, care was taken to rule out the possibility that II gives IV by a *cis*

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[1] For paper VII in this series see F. G. Bordwell and P. S. Landis, This Journal, **79**, 1593 (1957).

[2] Socony–Mobil Predoctoral Fellow, 1956–1958.

[3] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[4] D. J. Cram, This Journal, **71**, 3883 (1949).

[5] (a) E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810, 3194 (1950); (b) **73**, 59 (1951).

[6] P. G. Stevens and J. H. Richmond, *ibid.*, **63**, 3132 (1941).

[7] D. H. R. Barton, *J. Chem. Soc.*, 2174 (1949).

[8] G. L. O'Connor and H. R. Nace, This Journal, **74**, 5454 (1952); **75**, 2118 (1953).

[9] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 462.

[10] A cyclic type mechanism was first suggested for ester pyrolyses by C. D. Hurd and F. H. Blunck, This Journal, **60**, 2419 (1938).

[11] (a) F. G. Bordwell and R. J. Kern, *ibid.*, **77**, 1141 (1955); (b) F. G. Bordwell and M. L. Peterson, *ibid.*, **77**, 1145 (1955); (c) F. G. Bordwell and J. Weinstock, *ibid.*, **77**, 6706 (1955).

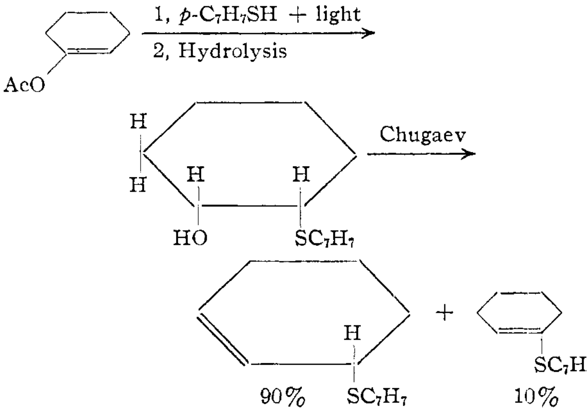
elimination followed by rearrangement of IV to III.[12]

The ultraviolet absorption spectrum of III has a maximum at 235 mμ, whereas the corresponding maximum for IV is at 226 mμ. Examination of synthetic mixtures showed that a shift of about 1 mμ in these maxima occurred for each 10% of isomer present, so that 10% of rearrangement could be detected readily. No rearrangement of IV to III occurred at the pyrolysis temperature (210°). Heating IV in 1-octanol (b.p. 194–195°) solution in the presence of an equimolar quantity of *p*-toluenesulfonic acid for one hour also failed to cause rearrangement. When treated with an equimolar quantity of potassium *t*-butoxide in *t*-butyl alcohol for 6 hours, III rearranged to IV to the extent of about 20%[13]; the amount of IV did not increase appreciably during another 16-hour reflux period. Under similar conditions IV was rearranged slowly to III, 50% rearrangement occurring in 6 hours and a mixture containing about 25% IV and 75% III was obtained after 22 hours. It seems likely that at equilibrium about 20% IV and 80% III are present.

The above experiments rule out any possibility of III being formed in the Chugaev reaction by way of IV since the rearrangement of IV to III does not occur at the pyrolysis temperature, even in the presence of concentrations of acid high relative to those likely to be present in the pyrolysis. If the product had been formed by rearrangement, about 20% of IV should have been present, but the Chugaev product contained less than 10% of this isomer. Finally, IV when added to the pyrolysis mixture did not rearrange to III, showing that there is no catalyst present which will effect this transformation.

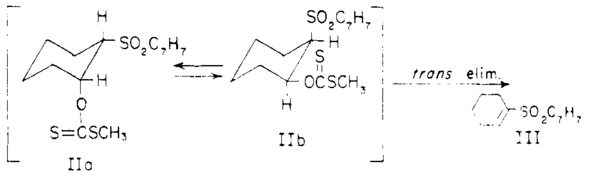
It seemed of interest to extend the study to the pyrolysis of the xanthantes of *trans*- and *cis*-2-*p*-tolylthiocyclohexanol in order to compare the effects of the weakly electron-withdrawing group C_7H_7S– with the strongly electron-withdrawing $C_7H_7SO_2$– group. The required *trans*-?-*p*-tolylthiocyclohexanol is readily available.[11a] The desired *cis* isomer was prepared by a light and/or peroxide initiated addition of *p*-thiocresol to cyclohexenyl acetate followed by hydrolysis. The *cis* structure of the product was established by oxidation to *cis*-2-*p*-tolylsulfonylcyclohexanol.[11c] The selective formation of *cis* products by free radical addition of *p*-thiocresol to olefins has been observed previously.[14]

Pyrolysis of the S-methyl xanthate of *trans*-2-*p*-tolylthiocyclohexanol (V) gave predominantly 1-*p*-tolylthio-1-cyclohexene, whereas pyrolysis of the *cis*-S-methyl xanthate VI gave largely 3-*p*-tolylthio-1-cyclohexene. Both of these can be formulated as *cis* eliminations occurring in the usual manner. The infrared spectrum of the pyrolysis product from V gives some evidence for the presence of 1-*p*-tolylthio-1-cyclohexene (estimated to be no more than 10%), which is presumably formed by a *trans* elimination.



Discussion

trans Chugaev eliminations can be visualized as occurring by several routes. Using the conversion of II to III as an example, intermolecular *trans* elimination *via* conformation IIa or intramolecular *trans* elimination *via* conformation IIb may be considered.[15] An intermolecular E2 type elimination is unlikely in view of our observation of first-order kinetics, although these data are admittedly rough. A concerted intramolecular *trans* elimination involving conformation IIb is improbable,[7] since this presumably would lead to the highly strained *trans* form of III, or would require considerable movement of atoms in the transition state. However, a *step-wise* intramolecular mechanism involving conformation IIb is acceptable sterically and is particularly attractive in this instance, since both negative and positive charges in the intermediate dipolar ion can be distributed over several atoms by resonance, as indicated.



The course of ester pyrolyses appears to be governed by three principal factors: (1) the acidity of the β-hydrogen,[16] (2) the stability of the olefin formed,[17] and (3) preference for a concerted reaction path where bond-making can assist bond-

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[12] The Chugaev reaction has proved useful for the conversion of alcohols to olefins without rearrangement in many instances where acid-catalyzed dehydrations lead to extensive rearrangements [see, for example, F. C. Whitmore and C. T. Simpson, THIS JOURNAL, **55**, 3809 (1933)]. A recent example is the conversion of *trans*-2-phenylcyclohexanol to 1-phenylcyclohexene in good yield *via* the xanthate,[5a] whereas phosphoric acid dehydration gives mainly rearrangement products [H. J. Schaeffer and C. J. Collins, *ibid.*, **78**, 124 (1956)]. In view of this, the statement by W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956), that "rearrangements are common" does not seem to be justified, particularly since no supporting examples of rearrangements during a Chugaev reaction were given.

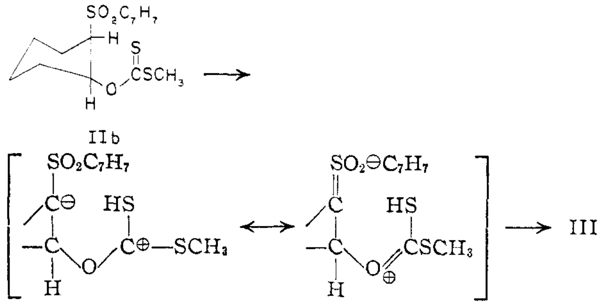
[13] Prof. H. E. Zimmerman and Dr. B. S. Thyagarajan observed a similar rearrangement for 1-benzenesulfonylcyclohexene to 3-benzenesulfonylcyclohexene and we are indebted to them for calling this to our attention.

[14] H. L. Goering, P. L. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1956); F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957).

[15] Conformation IIa, which places the large [see F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5184 (1951); J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3468 (1956)] *p*-tolylsulfonyl group in an equatorial position should be more stable than IIb.

[16] See W. J. Bailey and C. King, *J. Org. Chem.*, **21**, 858 (1956).

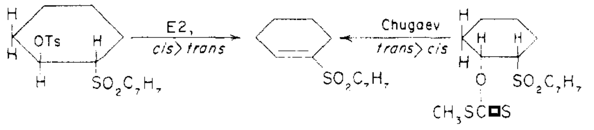
[17] See C. H. DePuy and R. E. Leary, THIS JOURNAL, **79**, 3705 (1957).



Dipolar intermediate

breaking.[3–8] In cyclic systems the latter is usually the dominant factor. For example, pyrolyses of the S-methyl xanthate or acetate of *cis*-2-phenylcyclohexanol[5a] and the S-methyl xanthate of *cis*-2-*p*-tolylthiocyclohexanol (VI) give mainly the non-conjugated olefins (*cis* eliminations involving the less acidic β-hydrogens to give the less stable olefins). If, however, the β-hydrogen is made strongly acidic it appears that *trans* elimination (by a non-concerted process) may be preferred to a *cis* elimination (concerted) which involves a non-acidic β-hydrogen. The stability of the olefin formed should not be important in the *trans* elimination if formation of a dipolar intermediate, such as that written above for the transformation of II → III, is rate determining. *trans* eliminations of this type can perhaps occur on pyrolysis of esters such as the xanthates or acetates of *cis*-2-methyl-1-tetralol[5b] and *cis*-2-methyl-1-indanol,[5a] where *cis* elimination is impossible, and to a minor extent in ordinary ester pyrolyses.[3,18]

It is interesting to note that sufficient activation of β-hydrogens in cyclic systems can cause the direction of both E2 and pyrolytic eliminations to be dictated by electronic rather than steric considerations.



Experimental[19]

Preparation and Pyrolysis of *trans*-2-*p*-Tolylsulfonylcyclohexyl S-Methyl Xanthate (I).—*trans*-2-(*p*-Tolylsulfonyl)-cyclohexanol[11a] (10.2 g., 0.04 mole) was added to 1.6 g. of potassium suspended in 100 ml. of dry toluene. The mixture was stirred for 1.5 hr., excess carbon disulfide (7.6 g.) was added and the reactants were stirred for 6 hr. at 40°. Methyl iodide (10 g.) was then added and the solution stirred overnight. The next day the solution was filtered and the filtrate washed thoroughly with water. The toluene was removed *in vacuo* leaving 13.5 g. of a viscous orange residue. Heating this residue at 210–215° under 1.5 mm. of pressure gave smooth decomposition with 7.2 g. (77%) of viscous oil distilling at 182–185°. This oil solidified on standing, giving material melting at 75–79°. One crystallization from hexane gave material melting at 80–81°, which did not depress the melting point of an authentic sample of 1-*p*-tolylsulfonyl-1-cyclohexene,[11a] $\lambda_{\max}^{\mathrm{KBr}}$ 3.40(m), 6.05(m), 6.22(s), 6.65(m), 6.85(s), 6.95(m), 7.00(m), 7.20(m), 7.40(w), 7.60(s), 7.65(s), 7.75(s), 8.70(s), 9.12(m), 9.44(m), 9.80(s), 10.25(w), 10.58(m), 10.72(m), 10.88(w), 11.70(m), 12.22(s), 12.50(m), 13.45(s), 14.12(s), 15.00(s). The infrared spectrum of the crude product failed to show peaks at 8.05(m), 10.02(m), 11.30(m), 11.45(m), 12.85(m), 13.63(m), which are characteristic of 3-*p*-tolylsulfonyl-1-cyclohexene.

Pyrolysis of *cis*-2-*p*-Tolylsulfonylcyclohexyl S-Methyl Xanthate (II).—A 2.02-g. sample of *cis*-2-*p*-tolylsulfonylcyclohexanol[11c] gave 2.91 g. of the methyl xanthate by the above procedure. Pyrolysis at 210–215° at 2.5 mm. pressure gave 1.5 g. (79%) of oil distilling at 180–190°. On standing, this oil crystallized giving material melting at 66–72°. Recrystallization raised the melting point only slightly. Chromatographic separation of a 0.405-g. sample over silica gel using hexane and benzene as successive eluents gave 0.201 g. of pure 1-*p*-tolylsulfonyl-1-cyclohexene (III), m.p. 81–83°; 0.109 g. of low melting solid (which from infrared analysis appears to be a mixture of III and the starting alcohol), and 0.055 g. of an evil-smelling yellow oil which was not characterized.

***cis*-2-*p*-Tolylthio-1-acetoxycyclohexane.**—A mixture of 30 g. (0.214 mole) of cyclohexenyl acetate, 26.0 g. (0.21 mole) of *p*-thiocresol and 0.1 g. of di-*t*-butyl peroxide was irradiated at 45–55° for 36 hr. under a nitrogen atmosphere. The yellow solution was distilled through a 20-inch Vigreux column at 0.8 mm. and a fraction distilling at 140–144° was collected; weight 13 g. (23%), $n^{25}\mathrm{D}$ 1.5788.

Anal. Calcd. for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62. Found: C, 67.66; H, 7.90.

***cis*-2-*p*-Tolylthio-1-cyclohexanol.**—*cis*-2-*p*-Tolylthio-1-acetoxycyclohexane (7 g., 0.012 mole) was refluxed with a solution of 50 ml. of 20% aqueous sodium hydroxide and 20 ml. of ethanol for 3 hr. The solution was poured into 50 ml. of water and extracted with ether. The ether solution was dried over anhydrous magnesium sulfate, the ether removed on the steam-bath and the residue distilled under vacuum. The fraction boiling at 160–163° (0.6 mm.) weighed 5.2 g. (88%), $n^{25}\mathrm{D}$ 1.5802.

Anal. Calcd. for $C_{13}H_{18}OS$: C, 70.22; H, 8.16. Found: C, 70.47; H, 8.07.

Oxidation of a small sample with 30% hydrogen peroxide gave *cis*-2-*p*-tolylsulfonyl-1-cyclohexanol, m.p. 88–92°, which was shown by mixed m.p. and infrared analysis to be identical with an authentic sample.[11c]

Preparation and Pyrolysis of *trans*-2-*p*-Tolylthiocyclohexyl S-Methyl Xanthate (V).—*trans*-2-*p*-Tolylthio-1-cyclohexanol (5 g., 0.02 mole) was added to a stirred suspension of 1.17 g. of finely divided potassium in 50 ml. of dry toluene. After 3 hr. only a trace of potassium remained and this was removed with a wire. Five grams of carbon disulfide was added, the solution was stirred for 3 hr. and 10 g. of methyl iodide added. The solution was heated at 50° for 5 hr. and allowed to stand overnight. The solution was then filtered and the filtrate washed with two 50-ml. portions of distilled water. The toluene extract was separated and the solvent removed under vacuum to yield 6.4 g. of a yellow oil. Vacuum distillation of 5.2 g. of this residue (pot temperature, 190–210°) gave 2.8 g. of product distilling at 125–135° (0.9 mm.), $n^{25}\mathrm{D}$ 1.5851. An 0.8-g. portion of this fraction was heated for one hour at 80° in a solution of 10 ml. of acetic acid containing 2 ml. of 30% hydrogen peroxide. The solution was poured into ice-water and extracted with chloroform. Evaporation of the solvent left a viscous gum which crystallized on standing overnight; m.p. 55–67°. The infrared spectrum showed the material to be primarily 1-*p*-tolylsulfonyl-1-cyclohexene (III). The quantity of 3-*p*-tolylsulfonyl-*p*-cyclohexene (IV) present is less than 10% as judged from a comparison of the spectrum of the crude product with the spectra of known mixtures of the two olefins. Two recrystallizations from benzene–hexane gave nearly pure III, m.p. 79–81°.

Pyrolysis of *cis*-2-*p*-Tolylthiocyclohexyl S-Methyl Xanthate (VI).—A 2.5-g. sample of *cis*-2-*p*-tolylthio-1-cyclohexanol was converted to the methyl xanthate, as described above. Vacuum decomposition of the resulting yellow-orange viscous oil gave 1.1 g. of product (54%), b.p. 140–145° (1 mm.). Oxidation of 0.8 g. of this oil with 2.5 ml. of 30% hydrogen peroxide in 10 ml. of acetic acid at 70–75° and recovery of the sulfone as described above gave 0.7 g. of colorless crystals, m.p. 47–56°. The infrared spectrum showed this product to be primarily 3-*p*-tolylsulfonyl-1-cyclohexene. Comparison with the spectra of known mix-

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(18) An ionic type mechanism such as that suggested by C. C. Price and G. Berti [G. Berti, THIS JOURNAL, **76**, 1213 (1954)] for the pyrolysis of methyl sulfite esters also offers a plausible route for *trans* elimination during ester pyrolysis. This will be discussed in detail in the next paper in this series.

(19) Microanalyses were by Miss Hilda Beck.

tures indicated the presence of 5–10% of III. Recrystallization gave a nearly pure sample of 3-*p*-tolylsulfonyl-1-cyclohexene, m.p. 59–61°.[11a]

Attempts at Purification of Xanthates.—Freshly prepared xanthates of the sulfone and sulfide alcohols I, II, V and VI all resisted attempts at crystallization and purification. Working with *trans*-2-*p*-tolylsulfonylcyclohexanol as a model, several attempts at purification of the resulting xanthate were made. Important observations include (1) removal of the solvent from the reaction mixture using a steam-bath gave some decomposition to olefin; (2) attempted distillation of the xanthate gave complete decomposition to olefin at low pressures (0.2 mm.); (3) chromatography over activated silica failed to separate a small amount of alcohol from the xanthate.

To evaluate the relative amounts of xanthate present in the crude reaction products a simple distillation flask connected to three cold traps for collecting and weighing carbon oxysulfide and methyl mercaptan was set up. Decompositions were carried out in a nitrogen atmosphere. Using cholesterol xanthate, m.p. 125–128° (reported[8] m.p. 127.5–128°), 102–104 weight per cent. of the theoretical quantity of volatile decomposition products was observed. The xanthates of I and II on similar treatment gave 81 and 78 weight per cent. of theoretical carbon oxysulfide and methyl mercaptan, reflecting relative purities of about 80%.

Kinetics.—Relative reaction rates were determined by loss of weight for a specific xanthate in tared erlenmeyers immersed in an oil-bath maintained at 166 ± 2°. After a specific time interval at the indicated temperature the reaction flasks were quenched in cold benzene and reweighed. Comparative rates are then expressed in terms of percentage unreacted xanthate at specific time intervals. This is essentially the procedure of O'Conner and Nace.[8] Approximate first-order rate constants were obtained by plotting the logarithm of percentage unreacted xanthate against the time in minutes. The rate constant k is equal to $-2.303 \times$ slope of the line of this plot. The approximate first-order rate constant obtained in this way for *trans*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate was 10.2×10^{-3} min.$^{-1}$. For the *cis* analog the rate constant was 4.37×10^{-3} min.$^{-1}$.

Ultraviolet Absorption Measurements.—Ultraviolet absorption spectra of the α,β- and β,γ-unsaturated sulfones III and IV and mixtures of these two isomers were determined using a Beckman DK-2 recording spectrophotometer. Concentrations of 4×10^{-5} M compound in 95% ethanol gave convenient (60%) transmittance. The absorption maxima for the sulfones are 235 mμ for pure III and 226 for pure IV. The maxima for synthetic mixtures were: 234 for 90% III + 10% IV; 232 for 80% III + 20% IV; 230 for 60% III + 40% IV; 227 for 10% III + 90% IV.

Tests for Rearrangement. (1) **During Pyrolysis.**—Two and eight-tenths grams of 3-*p*-tolylsulfonyl-1-cyclohexene (IV) and 8.5 g. (0.0247 mole) of *trans*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate were mixed and placed in a 25-ml. distillation flask. The flask contents were heated under nitrogen for ten minutes at 220°, vacuum was applied and the product distilled slowly under 2 mm. vacuum. Seven and six-tenths grams of an oil, which slowly crystallized, was collected. The crude solid, 4×10^{-5} M in 95% ethanol, gave maximum ultraviolet absorption at 230 mμ indicating about 60% 1-olefin III and 40% 3-olefin IV. The product should contain about 65% III and 35% IV if no rearrangement occurs.

Refluxing 105 mg. (0.42 millimole) of IV with 80 mg. (0.42 millimole) of *p*-toluenesulfonic acid in 10 ml. of 1-octanol (b.p. 194–195°) also failed to cause rearrangement as measured by ultraviolet absorption. Refluxing 0.1 g. of potassium in 30 ml. of *t*-butyl alcohol with 1.05 g. of III for six hours caused rearrangement to the extent of about 20%; the amount of IV did not increase appreciably during another 16-hour reflux period with potassium *t*-butoxide in *t*-butyl alcohol. Under similar conditions 1.0 g. of IV and 0.1 g. of potassium in 30 ml. of *t*-butyl alcohol caused slow rearrangement to III, 50% rearrangement occurring in 6 hours and a mixture of 25% IV and 75% III was obtained after 22 hours. In all cases the products were isolated from the reaction mixture by the addition of cold water, extraction of the aqueous solution with chloroform, and evaporation of the solvent from the extract leaving the solid residues on which all ultraviolet absorption measurements were made directly.

(2) **Of *cis*-Alcohol During Salt Formation.**—One and six-tenths grams (0.007 mole) of *cis*-2-*p*-tolylsulfonyl-1-cyclohexanol in 20 ml. of dry benzene was stirred with 0.20 g. of metallic potassium for five hours. The benzene was removed under a stream of nitrogen and the mushy solid residue treated with 20 ml. of 5% HCl. The insoluble white solid was removed by filtration and washed with water and 5% HCl. The dried residue gave a m.p. of 85–89° and infrared analysis showed no evidence for formation of the *trans* isomer.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Hydrogen Bromide Cleavage of Hindered 2-Methoxyacetophenones

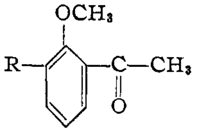
BY W. J. HORTON AND JACK T. SPENCE[1]

RECEIVED SEPTEMBER 9, 1957

The facile cleavage of 3-substituted-2-methoxyacetophenones is ascribed to the steric influence of the 3-substituent. The rate of cleavage of a number of such compounds has been determined and these data as well as ultraviolet spectra support the proposal of steric inhibition of resonance by the 3-substituent.

The room temperature cleavage of 2-alkoxyacetophenones by means of hydrogen bromide–acetic acid was shown previously to be promoted by a methoxy group in the 3-position, whereas a 5-methoxy group lacked this influence.[2] This facile cleavage was first observed in methoxybenzosuberones.[3]

In a kinetic study of the conversion of 2,3-dimethoxyacetophenone (I) to 2-hydroxy-3-methoxyacetophenone by means of hydrogen bromide–acetic acid it has been found that the reaction is first order with respect to I; that the order of the reaction is two and by inference, the reaction is first order with respect to hydrogen bromide. It was found that the rate of the reaction was greatly influenced by traces of moisture. In the cleavage of naphthol ethers[4] and anisole[5] by aqueous hydrohalogen–acetic acid, inhibition by increasing



I, R = OCH_3
II, R = CH_3

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[1] From the Doctoral Dissertation of Jack T. Spence.

[2] (a) W. J. Horton and J. T. Spence, THIS JOURNAL, **77**, 2894 (1955); (b) P. D. Gardner, W. J. Horton and R. E. Pincock, *ibid.*, **78**, 2541 (1956).

[3] P. D. Gardner and W. J. Horton, *J. Org. Chem.*, **19**, 213 (1954).

[4] G. P. Kolhatkar and V. V. Bapat, *J. Univ. Bombay*, **7**, Pt. 3, 157 (1938); *C. A.*, **33**, 5268 (1939).

[5] R. P. Ghaswalla and F. G. Donnan, *J. Chem. Soc.*, 1341 (1936).