change in *p*H is always slightly larger than would be expected on the basis of ion exchange, and the conductivity of the buffer in the trough increases slowly throughout the run, indicating that salt is accumulated in the starch medium. This accumulation of salt probably is due to swelling of the starch granules and consequent accumulation of salt inside the granule membrane due to the Donnan effect, although a decrease in the rate of migration of the buffer ions in the starch medium might also play a role. Evaporation seems to be excluded as a factor of any importance, since the effect is strongly dependent upon the type of buffer, being in general larger for buffers with a *p*H below 7 than for those with a *p*H above 7 (Table III).

Finally, it should be pointed out that since the mobility of a charged molecule varies in an inverse manner with the ionic strength of the medium, the relatively higher concentration of buffer ions in the starch might well, at least in part, be a contributing factor in the lowering of the mobility of proteins in this medium as compared with that of proteins in free solution at the same *p* H.

Acknowledgment.—The author wishes to thank Dr. J. Léonis for determination of the titration curve of starch and for valuable discussion and to express appreciation to Professor C. H. Li for his support and interest in the present investigation.

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BERKELEY 4, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

The Stereochemistry of Proton Transfer Reactions. VII[1]

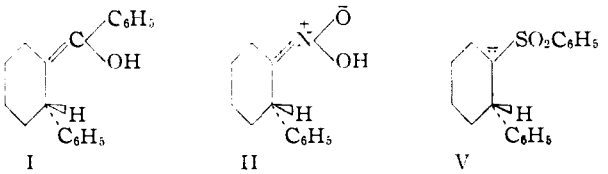
BY HOWARD E. ZIMMERMAN AND B. S. THYAGARAJAN

RECEIVED DECEMBER 7, 1957

The stereochemistry of protonation of the conjugate base of 1-benzenesulfonyl-2-phenylcyclohexane has been investigated. This has been found to lead, in sharp contrast to the behavior of the carbonyl and nitro analogs, preferentially to the more stable of two stereoisomeric products. This antithetical situation is considered to result from the difference in the energetic importance of electron delocalization in carbanions stabilized by the sulfone group as opposed to the carbonyl and nitro groups.

In previous studies of ketonization of enols[2] and tautomerism of *aci*-nitro to nitro compounds[3] it has been concluded that the proton transfer process occurs *via* an essentially sp^2 hybridized transition state with steric hindrance to protopic attack controlling the stereochemistry of the reaction under kinetically controlled conditions. This interpretation derives first from the observation that under non-equilibrating reaction conditions the less stable of two possible stereoisomers frequently results and, secondly, from a consideration of possible transition states leading to these products.

Thus, ketonization of the unstable enol I led stereoselectively to *cis*-1-benzoyl-2-phenylcyclohexane.[4] Similarly tautomerism of the *aci*-nitro compound II was found[3] to proceed by way of its conjugate base with formation of *cis*-1-nitro-2-phenylcyclohexane.



I II V

Of special interest was the stereochemistry of protonation of the related sulfone system V, not only as an integral part of our investigations into the mechanism of proton transfer reactions but also as a source of information which might bear on the nature of carbanion stabilization by the sulfone group. The particular system V was chosen for this study since considerable information was available from investigations[5] of the carbonyl and nitro analogs.

Needed for the study were: first, syntheses of *cis*- and *trans*-1-benzenesulfonyl-2-phenylcyclohexane and proof of their configurations; secondly, procedures for unambiguously preparing the conjugate base (V) of these; and finally, investigation of the stereochemistry of protonation of this conjugate base. As part of the first objective, *cis*-1-benzenesulfonyl-2-phenylcyclohexane (IVa) was conveniently prepared by free radical addition of thiophenol to 1-phenylcyclohexene followed by peracetic acid oxidation without purification of the intermediate phenyl 2-phenylcyclohexyl sulfide. The crude oxidation product was found by quantitative infrared analysis to consist of 92% *cis*-1-benzenesulfonyl-2-phenylcyclohexane (IVa) and only 8% of the *trans* isomer IVb. This stereochemical result represents support for the assigned configurations, since it has been shown by Bordwell[6] and Goering[7] that the free radical addition of thiols to 1-substituted cyclohexenes preferentially yields the *cis* product. Recrystallization of the crude sulfone product afforded pure *cis*-sulfone IVa, m.p. 120°, without difficulty.

As further evidence for the assigned configurations and as a convenient preparation of the

(1) Presented in part at the Organic Division, A.C.S. Meeting, New York, September, 1957.

(2) Paper VI of this series, Howard E. Zimmerman and Theodore W. Cutshall, THIS JOURNAL, **80**, 2893 (1958).

(3) Howard E. Zimmerman and Thomas E. Nevins, *ibid.*, **79**, 6559 (1957).

(4) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

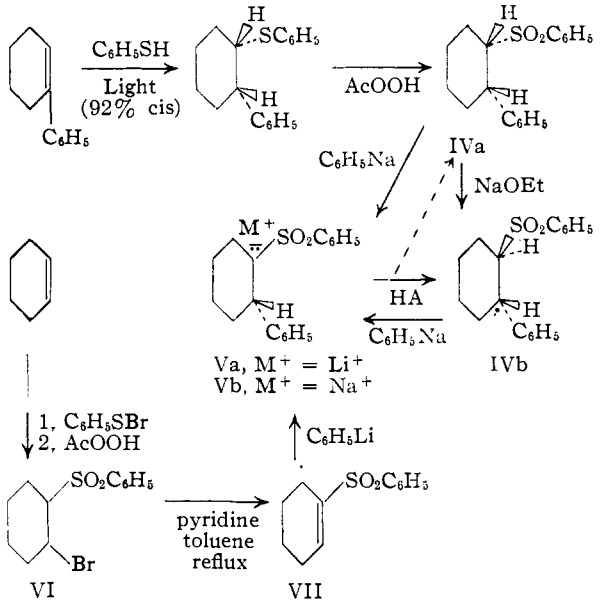
(5) See ref. 2 and earlier papers cited therein.

(6) F. G. Bordwell and W. A. Hewett, THIS JOURNAL, **79**, 3493 (1957).

(7) H. L. Goering, D. I. Relyea and D. W. Larson, *ibid.*, **78**, 348 (1956).

trans-sulfone IVb, *cis*-1-benzenesulfonyl-2-phenylcyclohexane (IVa) was refluxed with ethanolic sodium ethoxide until equilibrium was reached. The product was found by quantitative infrared analysis to consist of only 0.2% *cis*-sulfone and 99.8% *trans* isomer. Crystallization afforded *trans*-1-benzenesulfonyl-2-phenylcyclohexane, m.p. 153°

CHART I



Three approaches to the conjugate base V of the sulfones were utilized (note Chart I). The first two of these involved treatment of *cis*- and *trans*-1-benzenesulfonyl-2-phenylcyclohexane (IVa and IVb) in separate experiments with the strong base phenylsodium. The third approach consisted of addition of phenyllithium to 1-benzenesulfonylcyclohexene (VII). This compound was conveniently prepared by oxidation of the adduct of benzenesulfenyl bromide and cyclohexene to yield 1-benzenesulfonyl-2-bromocyclohexane, and then by β-elimination with pyridine. The structure assigned to VII is in accord with its ultraviolet spectrum which exhibits a strong maximum at 226 mμ (log ϵ 4.30).[8]

The conjugate base V thus obtained (Chart I) was protonated by addition to a solution of excess of the proton donor, and the sulfone product formed was analyzed by a quantitative infrared technique. The results of these experiments, in which various proton donors were employed and in which both benzene and tetrahydrofuran were used as solvents, are summarized in Table I.

Prior to discussion of the stereochemistry of the protonation reaction two important points must be established. First, it must be demonstrated that the three modes of anion generation described above do indeed lead to the carbanion V. Secondly, it must be certain that the protonation reactions are ionic, involving the carbanion, and do not proceed by an SEi mechanism[9,10] or some other stereospecific process.

TABLE I

Run	Conjugate base, salt	Solvent	Proton source	*cis*-Sulfone, %
1	Lithium	Tetrahydrofuran	Benzoic acid	26.4
2	Sodium[a]	Tetrahydrofuran	Benzoic acid	28.5
3	Sodium[b]	Tetrahydrofuran	Benzoic acid	28.9
4	Sodium[a]	Tetrahydrofuran	Phenol	14.6
5	Sodium[b]	Tetrahydrofuran	Phenol	14.7
6	Sodium[b]	Tetrahydrofuran	*o*-Cresol	28.7
7	Sodium[b]	Tetrahydrofuran	2,6-Xylenol	31.5
8	Sodium[b]	Tetrahydrofuran	2,6-Di-*t*-butylphenol	33.2
9	Sodium[b]	Tetrahydrofuran	*p*-Nitrophenol	29.2
10	Sodium[a]	Tetrahydrofuran	Hydrochloric acid	30.3
11	Sodium[b]	Benzene	Phenol	25.2
12	Sodium[b]	Benzene	2,6-Xylenol	21.9
13	Sodium[b]	Benzene	*p*-Nitrophenol	24.7
14	Sodium[b]	Water	Ammonium chloride	14.4
15	Lithium	Water	Hydrochloric acid	24.3

[a] Generated from the *cis*-sulfone. [b] Generated from *trans*-sulfone.

Evidence bearing on each of these problems is available from a consideration of the results obtained on protonation of carbanion V prepared by the three independent approaches (*vide supra*) but protonated under identical conditions. It may be seen (Table I, runs 1, 2 and 3) that within experimental error the product distribution resulting when carbanion V was protonated with benzoic acid in tetrahydrofuran was independent of the mode of generation of the carbanion. Similarly, the carbanion generated by reaction of phenylsodium with *cis*-1-benzenesulfonyl-2-phenylcyclohexane gave the same product distribution on protonation with phenol in tetrahydrofuran as was observed when the carbanion was derived from the *trans*-sulfone (Table I, runs 4 and 5). The lack of dependence of the stereoselectivity on the nature of the metal cation argues against an SEi replacement of metal by hydrogen and confirms the view that a relatively free carbanion is protonated. Furthermore, independence of the selectivity of the mode of generation, each one reasonably being expected[11] to yield V, is support for the common intermediate.

The most striking aspect of the results of the protonation experiments summarized in Table I is the preferential formation of the more stable *trans*-1-benzenesulfonyl-2-phenylcyclohexane (IVb) under all conditions. This contrasts with the preferred formation of the less stable ketone and nitro stereoisomers from the enol I[4] and *aci*-nitro II[3] analogs.[12] From this it may be concluded that

(8) The 200–240 mμ region is especially useful in determining the degree of conjugation of sulfones. C. C. Price and H. Morita (THIS JOURNAL, **75**, 4747 (1953)) have reported diphenyl sulfone to absorb at 235 mμ (4.2), phenyl vinyl sulfone at 225 mμ (4.2) and phenyl β-chloroethyl sulfone at 210 mμ (4.0). E. Fehnel and M. Carmack (*ibid.*, **71**, 231 (1949)) reported methyl phenyl sulfone to absorb at 217 mμ (3.83) and vinyl ethyl sulfone near 210 mμ (2.45). Thus compound VII may be seen to be the α,β-unsaturated rather than the β,γ-unsaturated isomer.

(9) S. Winstein, T. G. Traylor and C. S. Garner, THIS JOURNAL, **77**, 3741 (1955).

(10) B. Henbest, *Ann. Repts.*, 110 (1956).

(11) The *p*Ka of dimethyl sulfone has been estimated as 23 by K. F. Bonhoeffer and J. Hochberg, *Z. physik. Chem.*, **A184**, 419 (1939). That for cumene has been reported by W. K. McEwen, THIS JOURNAL, **58**, 1124 (1936), as 37. Thus the hydrogen atom alpha to the benzenesulfonyl group would be expected to be much more acidic than the next most susceptible hydrogen atom. Similarly, addition of phenyllithium to 1-benzenesulfonylcyclohexene as pictured has literature analogy in the work of E. P. Kohler and H. Potter, *ibid.*, **57**, 1316 (1935); H. Potter, *ibid.*, **76**, 5472 (1954).

(12) The objection might be raised that protonation of the sulfone anion V is not analogous to the ketonization process and to *aci*-nitro-

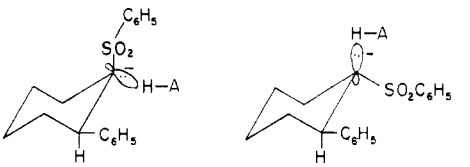
the transition state for protonation of the sulfone anion is not sp^2 hybridized as is the case for ketonization and *aci*-nitro tautomerism. Instead, the carbon atom bonding with the proton donor is essentially sp^3 hybridized. This is the situation described by Barton[13] for protonation of nonresonance stabilized carbanions. However, in the case discussed by Barton, not only the transition state and product are tetrahedral, but this is true of the carbanion reactant itself as well. While the transition state and product in the sulfone anion protonation are sp^3 hybridized, this appears not to be true of the carbanion reactant V. Doering[14] has presented evidence that sulfone carbanions are sp^2 hybridized and stabilized by d–p overlap rather than by an inductive effect. Bordwell[15] has presented independent evidence for resonance interaction by the sulfone group. Thus the antithesis between the enol and *aci*-nitro situation and that of the sulfone seems most probably to be attributable to factors other than ground state geometry.

Similarly, it seems unlikely that a later transition state[16] is responsible, for the conversion of the sulfone anion (pK_a conj. acid *ca.* 23) to sulfone is a much more highly exergonic and probably exothermic reaction than the conversion of the *aci*-nitro anion (pK_a conj. acid *ca.* 8.5[17]) to the nitro tautomer.

To rationalize the observed stereochemistry in light of these considerations it may be concluded that, while the sulfone anion is very likely resonance stabilized and hence sp^2 hybridized, delocalization of the electron pair on the α-carbon atom is energetically less important than in the analogous nitro and keto stabilized carbanions. Thus, when the transition state has been attained, these electrons are largely localized in a newly developed sp^3 orbital with partial overlap with the s orbital of the bonding proton. Of the two possible transition states VIIIa and VIIIb the latter, leading to the *trans* product, is preferred since the steric requirements of the benzenesulfonyl group are more demanding than those of the proton and the more distant proton carrier, and the benzenesulfonyl group is equatorially bonded.

Also of considerable interest is the dependence of the stereoselectivity on the nature of the proton donor and the solvent employed for protonation. It may be seen that the percentage of *cis* isomer increases with increasing bulk of the proton donor. Thus in tetrahydrofuran an increasing amount of *cis*-sulfone is observed with the series of proton donors phenol < *o*-cresol < 2,6-xylenol < 2,6-di-*t*-butylphenol.[18] Also, there is an increase in *cis* product with increasing acidity of the proton donor in tetrahydrofuran and in water. Thus the selectivity obtained with hydronium ion (run 15) is greater than with the weaker acid ammonium ion (run 14); likewise, in tetrahydrofuran more *cis*-sulfone results from protonation by *p*-nitrophenol (pK_a 7.76[20]) than with the weaker acid phenol (pK_a 9.99[20]).

The effect of the size of the proton donor on the selectivity is reasonable, for as its steric demands increase, the energy of transition state VIIIb will also increase. The effect of acidity of the proton donor on the selectivity may be attributed to an earlier transition state with the stronger acids with



VIIIa VIIIb

less complete attainment of sp^3 hybridization and a consequent decreased importance of the bulk of the benzenesulfonyl group and increased importance of the requirements of the proton donor.

Experimental[21]

Phenyl 2-Bromocyclohexyl Sulfide.—To a suspension of 144.4 g. (0.81 mole) of N-bromosuccinimide in 300 ml. of anhydrous benzene was added with stirring under rigorously anhydrous conditions 90.6 g. (0.82 mole) of thiophenol in 600 ml. of anhydrous benzene. The reaction which ensued was exothermic with the development of an intense red color. Occasional cooling was necessary to moderate the reaction. The mixture was stirred for 15 minutes after completion of the addition.

The solution of benzenesulfenyl bromide thus formed was siphoned through a filter stick with the use of positive nitrogen pressure into a stirred solution of 164 g. (2 moles) of cyclohexene in 200 ml. of anhydrous benzene. An exothermic reaction followed with the rapid disappearance of the red color of benzenesulfenyl bromide. At the end of the addition the mixture was stirred for an additional 5 minutes. Concentration *in vacuo* left 159.5 g. of phenyl 2-bromocyclohexyl sulfide as a thick oil which could not be distilled; this was used directly for the following preparation.

1-Benzenesulfonyl-2-bromocyclohexane.—To a solution of 20.0 g. of phenyl 2-bromocyclohexyl sulfide in 50 ml. of acetic acid was added with stirring and cooling 100 ml. of 40% (Becco) peracetic acid at a rate such that the temperature remained below 40°. The addition required 20 minutes. The mixture was then allowed to stand for 2 hours. Water then was added slowly to the mixture. The crystalline solid which separated was filtered, washed and dried

nitro tautomerism. However, the latter process has been shown (ref. 3) to proceed by protonation of the conjugate base of the nitro compound as seems likely for protonation of the sulfone anion V and hence the analogy is correct. No evidence is to be found in the literature for existence of species isomeric with sulfones and analogous to enolic and *aci*-nitro intermediates.

(13) D. H. R. Barton and C. Robinson, *J. Chem. Soc.*, 3045 (1954).

(14) W. v. E. Doering and L. K. Levy, THIS JOURNAL, **77**, 509 (1955).

(15) F. G. Bordwell and H. M. Anderson, *ibid.*, **75**, 6019 (1953).

(16) It is necessary to define the basis of the reaction coördinate. It is true that in terms of bond angles the sulfone protonation transition state would appear to occur later than the sp^2 transition states of ketonization and *aci*-nitro tautomerism where the hybridization has not appreciably changed in proceeding from ground to transition state. A better measure of the extent of reaction is bond order of bonds being formed and broken.

(17) D. Turnbull and S. H. Maron, THIS JOURNAL, **65**, 212 (1943), have reported a pK_a of 8.46 for 2-nitropropane, a reasonable model compound for the conjugate acid of II.

(18) This trend seems most reasonably attributed to a steric effect, since the acidities of the phenols concerned are quite close: phenol pK_a 9.85 (ref. 19), 9.99 (ref. 20); *o*-cresol 10.06 (ref. 19); 2,6-xylenol 10.58 (ref. 20). The actual donor involved in protonation seems most likely to be a phenol–tetrahydrofuran hydrogen bonded species in THF. In benzene the phenols are fairly certainly associated to varying degrees (K. Endo, *Bull. Chem. Soc. Japan*, **1**, 25 (1926); the decreased *cis*-isomer formed with 2,6-xylenol in this solvent may be due to a lesser degree of association because of steric hindrance.

(19) O. Grawton, M. Duggan and C. J. Grelecki, *Anal. Chem.*, **24**, 969 (1952).

(20) G. W. Wheland, R. M. Brownell and E. C. Mayo, THIS JOURNAL, **70**, 2492 (1948).

(21) All melting points were taken on a Fisher–Johns block checked with known compounds.

to yield 15 g. of product melting at 59°. Recrystallization brought the melting point of the 1-benzenesulfonyl-2-bromocyclohexane to 62°.

Anal. Calcd. for $C_{12}H_{15}SO_3Br$: C, 47.57; H, 4.99. Found: C, 47.27; H, 4.70.

1-Benzenesulfonylcyclohexene.—A solution of 16.0 g. of 1-benzenesulfonyl-2-bromocyclohexane in 80 ml. of toluene and 80 ml. of anhydrous pyridine was refluxed for 4.5 hours at the end of which time no additional pyridinium bromide separated. The cooled mixture was washed with water and then with dilute hydrochloric acid and finally with water. The toluene solution was then dried over sodium sulfate. Concentration under vacuum left 11.7 g. of a sticky solid which tended to oil on crystallization. However, cooling with ice of a solution of the compound in a minimum of ether followed by addition of just enough pentane to leave a permanent cloudiness led to crystallization of pure 1-benzenesulfonylcyclohexene, m.p. 46–47°. The melting point was not altered by further crystallization. The ultraviolet spectrum in 95% ethanol exhibited a maximum at 226 mμ (log ε 4.30).

Anal. Calcd. for $C_{12}H_{14}SO_2$: C, 64.86; H, 6.31. Found: C, 64.63; H, 6.15.

***trans*-1-Benzenesulfonyl-2-phenylcyclohexane; Addition of Phenyllithium to 1-Benzenesulfonylcyclohexene.**—To a stirred suspension of 0.21 g. of lithium in 10 ml. of anhydrous ether was added a solution of 2.15 g. of bromobenzene in 10 ml. of anhydrous ether at such a rate to maintain steady reflux. After stirring for 45 minutes, a solution of 2.0 g. of benzenesulfonylcyclohexene in 10 ml. of anhydrous ether was added slowly over 10 minutes. The mixture became warm and brownish yellow. After stirring for a half-hour at room temperature, the mixture was poured into ice and saturated ammonium chloride solution. The white solid was filtered, washed with water and dried to give 2.18 g. of product melting between 95 and 140°. Recrystallization from chloroform–ether gave 1.7 g. of material melting sharply at 153°. Further crystallization did not raise the melting point.

Anal. Calcd. for $C_{18}H_{20}SO_2$: C, 72.00; H, 6.67. Found: C, 71.67; H, 6.45.

***cis*-1-Benzenesulfonyl-2-phenylcyclohexane.**—A mixture of 11.0 g. (0.10 mole) of thiophenol and 15.8 g. (0.10 mole) of 1-phenylcyclohexene, prepared by the potassium bisulfate dehydration of 1-phenylcyclohexanol, was irradiated with a Hanovia immersion type ultraviolet source for 48 hours at room temperature. The mixture was distilled at 0.01 mm. and the fraction boiling at 140–160° weighed 11.0 g. and represented a mixture of the stereoisomeric phenyl 2-phenylcyclohexyl sulfides.

This product (11.0 g.) was dissolved in 40 ml. of acetic acid and to the stirred solution was added 60 ml. of 40% peracetic acid at a rate such that the temperature did not exceed 40°. After an additional two hours the reaction mixture was treated with water to yield 9 g. of crude sulfone, m.p. 95–120°. Quantitative infrared analysis indicated this material to consist of 91.9% *cis* stereoisomer and 8.1% *trans* isomer. Recrystallization of the crude product from methanol afforded 7 g. of pure *cis*-1-benzenesulfonyl-2-phenylcyclohexane, m.p. 120°. Further crystallization did not raise the melting point.

Anal. Calcd. for $C_{18}H_{20}SO_2$: C, 72.00; H, 6.67. Found: C, 71.87; H, 6.42.

Equilibration of *cis*- and *trans*-1-Benzenesulfonyl-2-phenylcyclohexanes.—To a sodium ethoxide solution prepared from 0.15 g. of sodium and 50 ml. of absolute ethanol was added 0.50 g. of *cis*-1-benzenesulfonyl-2-phenylcyclohexane. The solution was refluxed for 24 hours, diluted with water and the precipitated material filtered and washed. The dried product weighed 0.49 g. Quantitative infrared analysis showed this to consist of 0.02% *cis* isomer, the remainder being *trans*.

When 0.30 g. of *cis*-1-benzenesulfonyl-2-phenylcyclohexane was refluxed for only 6 hours with a solution of sodium ethoxide prepared from 0.06 g. of sodium and 30 ml. of ethanol, the product weighing 0.27 g. analyzed as 7.5% *cis* isomer, equilibrium not being established.

When 100 mg. of *trans*-1-benzenesulfonyl-2-phenylcyclohexane was refluxed for 6 hours with a solution of sodium ethoxide prepared from 0.020 g. of sodium and 10 ml. of ethanol, the product obtained by dilution with water weighed 0.09 g. and proved to be unchanged *trans* isomer.

Protonation of the Conjugate Base of 1-Benzenesulfonyl-2-phenylcyclohexane Obtained with Phenylsodium.—To 10 ml. of isoöctane in a 100-ml. Morton flask was added 0.46 g. of sodium. By means of refluxing and high speed stirring the sodium was dispersed. The mixture was then cooled. To this was added 1.13 g. of chlorobenzene in 10 ml. of anhydrous benzene dropwise over 20 min. followed by stirring at room temperature for an additional two hours. To the resulting suspension of phenylsodium was added a warm solution of 2.00 g. of *trans*-1-benzenesulfonyl-2-phenylcyclohexane in 40 ml. of anhydrous benzene. The mixture was then stirred for 2.5 hours giving a green suspension of the conjugate base. At the end of this time the reaction mixture was poured into 75 ml. of tetrahydrofuran containing 3.0 g. of benzoic acid with high speed stirring. After stirring for 10 minutes, the product was isolated by dilution with water and chloroform extraction. The extracts were washed with 100 ml. of saturated sodium bicarbonate solution, with water, and then dried over sodium sulfate and concentrated *in vacuo*. Infrared analysis of the residue indicated 26.4% *cis*-1-benzenesulfonyl-2-phenylcyclohexane.

When this experiment was repeated using *cis*-1-benzenesulfonyl-2-phenylcyclohexane for generation of the sulfone conjugate base, the reaction product analyzed as 28.5% *cis* isomer.

Protonation of the Conjugate Base of 1-Benzenesulfonyl-2-phenylcyclohexane Obtained by the Addition of Phenyllithium to 1-Benzenesulfonylcyclohexene.—The addition of phenyllithium to 1-benzenesulfonylcyclohexene was carried out exactly as described above in the preparation of *trans*-1-benzenesulfonyl-2-phenylcyclohexane. The lithium salt thus obtained was poured into a solution of 3.0 g. of benzoic acid in 75 ml. of tetrahydrofuran with high speed stirring. After several seconds white solid separated with complete decolorization of the brownish-yellow ether solution. Stirring was continued for 10 minutes. Then the product was isolated by dilution with water, chloroform extraction, washing of the extracts with 100 ml. of saturated sodium bicarbonate solution, drying over sodium sulfate and concentration. The residue weighed 2.30 g. Quantitative analysis indicated 26.4% *cis*-1-benzenesulfonyl-2-phenylcyclohexane.

Procedures for Protonation of the Conjugate Base by Other Proton Donors.—For these experiments the conjugate base of 1-benzenesulfonyl-2-phenylcyclohexane was prepared by reaction of *trans*-1-benzenesulfonyl-2-phenylcyclohexane with phenylsodium as described above. The dispersion of the conjugate base was then added to a solution containing an excess (3.0 g.) of the proton donor in 75 ml. of the given solvent, tetrahydrofuran or benzene. The products were isolated as described above for protonation by benzoic acid except that proton donors weaker than benzoic acid were removed by alkali extraction under conditions where the *cis*-sulfone was not isomerized. The products were then analyzed by quantitative infrared spectra. The results are summarized in Table I.

TABLE II

Actual % *cis* isomer	*D'*	*D''*	*Q*	Actual *R*	Calcd. *F*	Calcd. *R*	Calcd. % *cis* isomer
100.0	0.537	0.0915	..	..	...	..	..
74.4	.488	.161	2.95	2.91	0.987	2.84	73.8
50.8	.347	.190	1.11	1.03	.929	1.06	51.6
26.5	.237	.237	0.372	0.361	.971	0.357	26.4
0.0	.131	.297	...	...	...	...	..

When the adduct of phenyllithium and 1-benzenesulfonylcyclohexene, prepared as described above, was poured into saturated aqueous ammonium chloride solution containing a small amount of ice, a white solid separated. This was filtered and washed with water to yield 2.18 g. of product melting at 95–140°. Recrystallization from chloroform–ether gave 1.7 g. of *trans*-1-benzenesulfonyl-2-phenylcyclohexane, m.p. 153°. When the crude product of an identical run was subjected to infrared analysis, this was found to consist of 14.9% *cis*-sulfone.

Quantitative Infrared Analysis.—The method described previously,[2] in which the ratio of *cis* to *trans* isomer, *R*, is given by the equation $R = QF$, was used. Here Q =

$\frac{D_t'D_m'' - D_t''D_m'}{D_c''D_m' - D_c'D_m''}$ and F is determined empirically from the calibration data in Table II. D_t, D_c and D_m are optical densities of pure *trans* isomer, pure *cis* isomer and a given mixture, respectively. The superscripts refer to absorption at the analytical wave lengths 13.40 μ(') and 13.53 μ('). The analytical solutions were in carbon disulfide and 2.0 mm. infrared cells were used. The optical density was taken to be zero at 11.0 μ. The total concentration used was 42 ± 2 mg./10.0 ml. of CS_2. The average value of F = 0.962 was used in calculating the results in the last two columns of Table II. The calibration runs in Table II indicate an estimated maximum error of ±0.8% *cis* isomer due to infrared uncertainties.

Acknowledgment.—The authors wish to express their gratitude to the Alfred P. Sloan Foundation for support of this research.

EVANSTON, ILLINOIS

[CONTRIBUTION NO. 168 FROM THE RESEARCH CENTER, UNITED STATES RUBBER CO.]

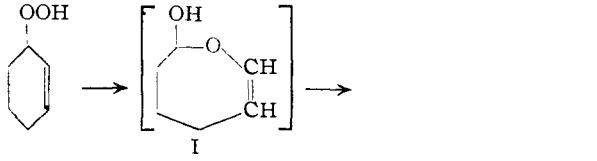
The Oxidation of Hydrocarbons. I. The Oxidation of Cyclohexene in Acetic and Propionic Anhydride Solutions[1]

BY HENRY J. SHINE[2] AND ROBERT H. SNYDER

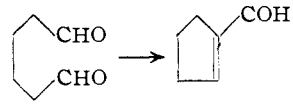
RECEIVED NOVEMBER 22, 1957

Cyclohexene has been oxidized at several temperatures in the range 25 to 80° in both acetic and propionic anhydride solutions by oxygen under free-radical initiation. Among the products isolated were the hitherto unknown esters, 3-oxa-4-cycloheptenyl acetate and propionate. These esters are stable over long periods of time in stoppered vessels. Detailed work on the acetic anhydride case has shown that cyclohexyl acetate also is formed. The nature of the oxidation is discussed.

The oxidation of cyclohexene and the decomposition of cyclohexene hydroperoxide[3] have been the subjects of many investigations. Among the products obtained are adipaldehyde (II) and cyclopentene-1-carboxaldehyde (III). It is customary to interpret[3] the formation of these aldehydes as arising from the decomposition of the cyclic intermediate I. This intermediate, however, never has been isolated, and no further evidence for its formation exists.

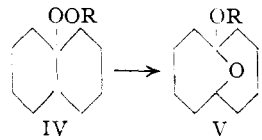


I



II III

Cyclic compounds similar to the type I are not unknown in peroxide chemistry. For example, the esters IV of decalin hydroperoxide have been shown by Criegee[4,5] to rearrange to the corresponding cyclic hemiacetal esters V.

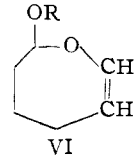


IV V

R = CH_3CO–, C_6H_5CO–, p-$NO_2C_6H_4CO$–

In the case of cyclohexene no peresters analogous to IV are known,[6] so that the preparation of esters analogous to V and corresponding with the parent compound I has not hitherto been possible.

As a consequence of work on the autoxidation of hydrocarbons we are now able to report the preparation of the esters VI by the oxidation of cyclohexene in acetic anhydride and in propionic anhydride. These esters are obtained in about 25% yield.



VI

VIa, R = CH_3CO–
VIb, R = CH_3CH_2CO–

Assignment of the structure VI to the esters is based on work with VIa: Treatment with hydroxylamine hydrochloride gave the dioxime of adipaldehyde. This apparently involves hydrolysis of the ester followed by ring opening to adipaldehyde.

Treatment of VIa with acidified 2,4-dinitrophenylhydrazine gave the bis-2,4-dinitrophenylhydrazone of adipaldehyde and the 2,4-dinitrophenylhydrazone of cyclopentene-1-carboxaldehyde. The last compound apparently arises from the acid-catalyzed aldol condensation of adipaldehyde.

Oxidation of VIa by neutral potassium permanganate gave glutaric acid, apparently by oxidation of the double bond between positions 1 and 2 and oxidation at position 4.

Hydrogenation of VIa over Adams catalyst gave 1,6-hexandiol and acetic acid. Hydrogenation over palladium black gave the saturated ester VII. Treatment of VII with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of 6-hydroxyhexanal.

In the case of VIb the structure is assigned from analysis and from the formation of the 2,4-dinitro-

(1) Presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., Sept., 1957.

(2) Department of Chemistry, Texas Technological College, Lubbock, Texas. Please address requests for reprints to Library, U. S. Rubber Co., Research Center, Wayne, N. J.

(3) For pertinent references to these investigations, particularly the outstanding work of Farmer's group, reference should be made to the review by E. G. E. Hawkins, *Quart. Revs.*, **4** (1950), and to the discussion of autoxidation by W. A. Waters, "Chemistry of Free Radicals," 2nd ed., Oxford, Clarendon Press, 1948, pp. 226–258.

(4) R. Criegee, *Ber.*, **77**, 722 (1944).

(5) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).

(6) R. F. Naylor, *J. Chem. Soc.*, 244 (1945), reported obtaining a small amount of material, believed to be cyclohexenyl peracetate, by the action of ketene on cyclohexene hydroperoxide at −70°. The difficulty in isolating the perester was attributed to the ease with which it was believed to decompose to cyclohexenyl acetate.