Reduction of Azlactone Mixture to Benzoyl-DL-phenylalanine.—(A) A mixture of 10 g. of the above azlactone, m.p. 130–152°, 1.6 ml. of constant-boiling hydriodic acid, 3 g. of red phosphorus and 70 ml. of glacial acetic acid was heated under refluxing conditions for one hour. The hot reaction mixture was filtered, poured into 1 liter of water, the precipitate collected and dried to give 8.1 g. (75%) of benzoyl-DL-phenylalanine, m.p. 181–182.5° (lit.[28] yield 72%, m.p. 181°). (B) In a second experiment a mixture of isomers melting at 124–141° gave a 64% yield of recrystallized benzoyl-DL-phenylalanine, m.p. 181–183°, which was not depressed on admixture with an authentic sample of benzoyl-DL-phenylalanine, m.p. 183.5–185°, prepared by the benzoylation of the amino acid.

Condensation of Benzaldehyde with Benzoylsarcosine.—Benzoylsarcosine, 5.4 g., was allowed to react with 3 ml. of benzaldehyde in a mixture of 3 ml. of 100% sulfuric acid and 9 ml. of acetic anhydride. The reaction mixture was allowed to stand for 24 hours at room temperature, the orange solution poured into 50 ml. of ice-water, the pale tan taffy collected, triturated with aqueous sodium carbonate solution, the alkaline solution extracted with ether and the ethereal extract discarded. The alkaline aqueous phase was acidified with concd. hydrochloric acid to give a pale yellow oil which was taken up in 65 ml. of chloroform and the chloroform solution was dried and filtered. The addition of 150 ml. of petroleum ether (60–70°) to the above solution precipitated a colorless oil, which solidified when the mixture was cooled in an ice-bath. The colorless solid was collected and dried to give 5.2 g. (66%) of α-(N-methylbenzamido)-cinnamic acid, m.p. 116–117.5° (lit.[29] m.p. 110–111°).

Anal. Calcd. for $C_{17}H_{15}O_3N$: C, 72.6; H, 5.4; N, 5.0. Found: C, 72.5; H, 5.3; N, 4.9.

Reaction of Benzoylglycine with Substituted Benzaldehydes.—The following aldehydes were condensed with benzoylglycine in a mixture of sulfuric acid and acetic anhydride essentially as described above. The crude products were treated with pyridine in the manner previously described. The yields and melting points of the corresponding azlactones were: anisaldehyde, 41%; m.p. 155.5–157.5° (lit.[56] m.p. 156.5°); *o*-chlorobenzaldehyde, 10%; m.p. 160–161° (lit.[57] m.p. 158–159°); *m*-nitrobenzaldehyde, 13%; m.p. 176–177° (lit.,[58] m.p. 178°). Salicylaldehyde gave a 76% yield of the triacetate, m.p. 98.5–100° (lit.[36] m.p. 101–102°).

Attempted Isomerization Reactions.—When 5 g. of 2-phenyl-4-benzal-5-oxazolone, m.p. 164–166°, was treated with 3 ml. of sulfuric acid and 9 ml. of acetic anhydride for 24 hours at room temperature 4.9 g. (98%) of the azlactone, m.p. 160–163°, was recovered. When 0.3 g. of an azlactone mixture, m.p. 123–129°, was heated for one-half hour at 100° with 5 ml. of acetic anhydride and 1 g. of sodium acetate, 0.3 g. (100%) of an azlactone mixture, m.p. 125–155°, was recovered.

Racemization of Benzoyl-D-alanine.—Benzoyl-D-alanine, large, glistening plates, m.p. 147–148°, $[\alpha]^{25}\text{D}$ −36.0° (0.9576 g. in 5 ml. aqueous sodium hydroxide), lit.[59] m.p. 148°, $[\alpha]^{25}\text{D}$ −36.9° (in an equivalent amount of aqueous potassium hydroxide) was used to prepare three solutions, *i.e.*, (A) 0.1429 g. in 5 ml. of 100% sulfuric acid; (B) 0.9426 g. and 1.25 ml. of 100% sulfuric acid made up to 5 ml. with acetic anhydride; and (C) 0.4382 g. in 10 ml. of acetic anhydride. The rotations of these three solutions as a function of time of standing at 25° are given in Fig. 2.

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(56) E. Erlenmeyer, Jr., and F. Wittenberg, *Ann.*, **337**, 294 (1904).

(57) F. Mauthner, *J. prakt. Chem.*, **95**, 55 (1917).

(58) H. Burton, *J. Chem. Soc.*, 1265 (1935).

(59) E. Pacsu and J. W. Mullen, *J. Biol. Chem.*, **136**, 335 (1940).

PASADENA 4, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

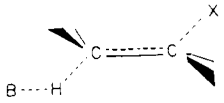
Mechanism of E2 Elimination Reactions. Stereospecificity of Elimination Reactions in the 2-Benzenesulfonyl-3-iodobutane System

BY PHILIP S. SKELL AND JAMES H. MCNAMARA

RECEIVED JULY 16, 1956

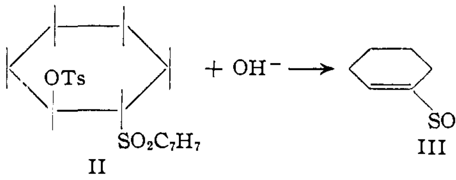
The base-catalyzed dehydrohalogenation of the two diastereoisomeric 2-benzenesulfonyl-3-iodobutanes is stereospecific. Thus, the presence of the powerful electron-withdrawing group, $C_6H_5SO_2$–, does not activate the H sufficiently to change the mechanism of E2 elimination (simultaneous loss of H and X) to one involving a carbanion intermediate.

The mechanism of base-catalyzed elimination reactions, E2, is generally considered to involve simultaneous loss of H and X and a planar transition state whose geometry corresponds to *trans* elimination.



I

Bordwell and Kern[1] have presented convincing evidence for E2 *cis*-elimination in the reaction of hydroxide ions with *trans*-2-(*p*-tolylsulfonyl)-cyclohexyl *p*-toluenesulfonate and the corresponding *trans*-cyclopentyl compound.



It was established that 3-*p*-tolylsulfonyl-1-cyclohexene (IV) was not an intermediate in the reaction which produces III. Thus II undergoes *cis*-elimination of *p*-toluenesulfonic acid to produce III in preference to the stereochemically favorable *trans*-elimination to produce IV. This enhancement of rate for *cis*-elimination was attributed to the acid-strengthening character of the sulfone substituent.

Two mechanistic sequences should be considered, (2) involving a carbanion intermediate, or (3) which

$$\underset{\text{II}}{RHX} + OH^- \rightleftharpoons RX^- + H_2O \qquad (2)$$

$$RX^- \longrightarrow \underset{\text{III}}{R} + X^-$$

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[1] F. G. Bordwell and R. J. Kern, THIS JOURNAL, **77**, 1141 (1955). This reference succinctly summarizes recent theoretical developments in this field. See also J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., N. Y., 1956, Chap. 7; D. J. Cram and F. A. Abd Elhafez, THIS JOURNAL, **74**, 5851 (1952); D. Y. Curtin and D. B. Kellom, *ibid.*, **75**, 6011 (1953).

$$\underset{\mathrm{II}}{\mathrm{RHX}} + \mathrm{OH}^- \longrightarrow \underset{\mathrm{III}}{\mathrm{R}} + \mathrm{H_2O} + \mathrm{X}^- \qquad (3)$$

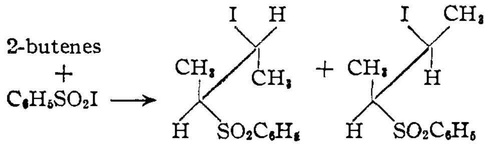
represents simultaneous removal of H and X requiring a *cis*-intermediate complex analogous to I.

In a later communication Weinstock, Pearson and Bordwell[2] indicated that the reactions for both the *cis* and *trans* isomers are general base rather than specific hydroxide catalyzed. From this evidence they conclude that if a carbanion intermediate is formed it must have a very short life (estimated $<10^{-8}$ sec.). However, Cristol and Fix,[3] found that starting material recovered from the base-catalyzed dehydrochlorination of β-benzene hexachloride (*trans*-elimination not possible) in deuteroethanol solvent contained deuterium. This evidence indicates the presence of a carbanion intermediate which on protonation can be converted to β-benzene hexachloride.

Both of these studies were complicated by the presence of cyclic structures which introduced the possibility of *a–e* isomerizations in both the starting materials and any intermediate carbanion. To avoid this complication the examination of a stereochemically simpler acyclic system was undertaken.

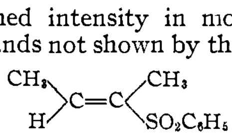
It was the purpose of this investigation to determine whether the acid-strengthening character of the sulfone substituent is large enough to change the concerted E2 mechanism of halogen acid elimination to one involving a carbanion intermediate. We chose for this study the two diastereomeric 2-benzenesulfonyl-3-iodobutanes.

The starting materials were prepared by the photochemical addition of benzenesulfonyl iodide to *cis*- or *trans*-2-butene. From either olefin, neither of which was isomerized during the reaction, an identical mixture of diastereomeric addition products was obtained.[4]

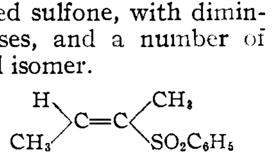


The identity of composition of the mixtures was indicated by the identity of infrared spectra and the fact that identical quantities of the solid isomer could be separated from either mixture. Although it was possible to obtain the solid isomer (m.p. 70.0–70.5°) in pure condition, the other isomer, which was apparently a liquid was not successfully purified. However, for this study the availability of one pure isomer and a mixture of the two isomers was sufficient.

Dehydrohalogenation of the solid isomer of 2-benzenesulfonyl-3-iodobutane with pyridine resulted in only one product, a solid unsaturated sulfone, m.p. 51°, which has been assigned one of the structures of the isomeric 2-benzenesulfonyl-2-butenes, (V) or (VI). Dehydrohalogenation of the liquid mixture of diastereomeric 2-benzenesulfonyl-3-iodobutanes under conditions identical to those employed with the solid isomer produced a mixture of unsaturated sulfones. The infrared spectrum of the mixture showed all the bands found in the spectrum of the solid unsaturated sulfone, with diminished intensity in most cases, and a number of bands not shown by the solid isomer.

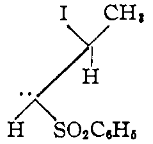


V



VI

This evidence supports the proposition that a different α,β-unsaturated sulfone is obtained from each of the isomeric 2-benzenesulfonyl-3-iodobutanes. Thus the dehydrohalogenation of these diastereomeric halides is a stereospecific reaction. It is possible to reject mechanistic sequence (2) for this reaction, since the formation of an intermediate carbanion would have resulted in identical mixtures of products from both diastereoisomers. These conclusions can be avoided only if the assumption is made that the carbanion loses a halide ion approximately ten times more rapidly than it suffers rotation about its central bond. Since the rates of rotation are estimated to be between 10^8 and 10^{12} sec.$^{-1}$, depending on the magnitude of the barrier, the life of the carbanion would have to be less than 10^{-9} sec. to explain the observed stereospecificity.[5]



Thus, in elimination reactions where no overpowering steric restrictions preclude *trans*-elimination, the separation of H and X from the parent molecule probably occurs simultaneously,[6] even in those cases where the hydrogen is activated by a powerful electron-withdrawing group.[7]

Experimental

Materials.—Benzenesulfonyl iodide was prepared by the reaction of iodine with sodium benzenesulfinate. The product was dissolved in carbon tetrachloride, dried over anhydrous sodium sulfate, and was used directly in this solvent. The benzenesulfonyl iodide content of these solutions was determined by treating an aliquot with excess ammonium hydroxide followed by argentometric titration of the liberated iodide ion. *cis*- and *trans*-2-butenes were Phillips Petroleum Co. Pure Grade hydrocarbons (99 mole % pure).

Photochemical Addition of Benzenesulfonyl Iodide to the *cis*- and *trans*-2-Butenes.—A number of paired experiments were carried out with these reactants. In a typical experiment 39.8 g. of benzenesulfonyl iodide (0.148 mole) and 28.8 g. of *cis*-2-butene (0.515 mole) in carbon tetrachloride solution (275 ml. of solution, Pyrex flask) was irradiated

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[2] J. Weinstock, R. G. Pearson and F. G. Bordwell, This Journal, **76**, 4748 (1954); **78**, 3468, 3473 (1956).

[3] S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953); also earlier references listed in this paper.

[4] For a discussion of the significance of these results see P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955).

[5] For details in an analogous discussion see P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

[6] P. S. Skell and C. R. Hauser, *ibid.*, **67**, 1661 (1945).

[7] The chemical literature contains examples at the opposite extreme, wherein steric restrictions are so large that in spite of ionization of a proton from an adjacent carbon atom, elimination of the halide ion is not observed. For example, P. D. Bartlett and S. G. Cohen, *ibid.*, **62**, 1183 (1940), reported that although the bicyclic β-bromo-*cis*-dicarboxylic acid, derived from the Diels–Alder reaction between maleic anhydride and 9-bromoanthracene, was isomerized to the *trans*-acid by hot aqueous potassium hydroxide, no elimination of bromide ion was observed. The *cis–trans* isomerization undoubtedly involves a carbanion intermediate.

at a distance of 6″ from a 200-watt incandescent tungsten filament lamp, while both lamp and flask were submerged in an ice-bath. During the first minute the temperature of the reactants rose to 26° and then slowly dropped to 0°. The reactants were irradiated for 35 minutes. Gas phase infrared spectra of the recovered olefins showed no detectable *cis–trans*-isomerization. In experiments where short irradiation periods were used, excess benzenesulfonyl iodide was removed by washing with an aqueous solution of potassium iodide and sodium bisulfite. Removal of solvent *in vacuo* left 48.7 g. (101% of theoretical yield based on benzenesulfonyl iodide) of liquid crude 2-benzenesulfonyl-3-iodobutanes, $n^{25}\mathrm{D}$ 1.582. Experiments in which *trans*-2-butene was used gave essentially identical results, no isomerization of unreacted olefin and a similar product, $n^{25}\mathrm{D}$ 1.586. The infrared spectra of the crude products from both olefins were superimposable when taken neat or in cyclohexane solvent.

In paired experiments 10.0 g. of each of these crude products was recrystallized from a solution of 80 ml. of *n*-heptane and 10 ml. of benzene to separate at 0° 3.46 and 3.45 g. of a solid product, respectively. The crude solids (m.p. 65.5–68.5°, mixed m.p. not depressed) had identical infrared spectra when taken in CS_2 solution ($\sim$ 1 g./100 ml. solution). Two recrystallizations from 95% ethanol raised the melting point to 70.0–70.5°, but did not change the infrared spectra noticeably. Attempts to separate the other isomer in pure condition were not successful.

The halogen content of the β-iodosulfones was determined argentometrically after liberating I^- by treating the sample with excess sodium methoxide solution (halogen-free). Calcd. for $C_{10}H_{13}SO_2I$: I, 39.1. Found for (a) crystalline isomer: I, 39.1; (b) crude product from *cis*-2-butene (VII): I, 38.5; (c) crude product from *trans*-2-butene (VIII): I, 36.8.

Infrared spectra of the pure solid isomer in CS_2 solution (1.50 g./100 ml. soln.) indicated absorption bands at 3.27, 3.36, 3.44, 7.25, 7.39, 7.58, 7.66, 7.80, 8.00, 8.08, 8.45, 8.67, 8.72, 9.20, 9.43, 9.75, 9.91, 10.01, 10.42, 11.90, 13.15, 13.50, 13.80, 14.48. The infrared spectra of the mixture of liquid isomers VII and VIII were identical and in CS_2 solution (2.21 g./100 ml. solution) showed all of the bands of the solid isomer and several additional bands. We list here only the new bands (indicated by *) and those bands which showed a larger extinction coefficient in the mixture. This procedure does not detect all of the bands of the liquid isomer. Some of the absorption bands of the liquid isomer appear at 7.25, 8.04*, 9.06*, 9.35*, 9.62*, 10.55*, 11.05*, 12.20*, 13.80, 14.45.

Dehydrohalogenation of the Diastereomeric 2-Benzenesulfonyl-3-iodobutanes.—The liquid mixtures of diastereoisomers were dehydrohalogenated by boiling under reflux with 10 g. of pyridine in 100 ml. of benzene. The pyridine was removed by washing with 10% hydrochloric acid and water, and the benzene solution was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was distilled at 1 mm. pressure through a 6″ Vigreux column.

The unsaturated sulfone prepared from 10 g. of VII was separated into two fractions: (1) b.p. 115°, $n^{25}\mathrm{D}$ 1.5542, 1.08 g.; (2) b.p. 115–117°, $n^{25}\mathrm{D}$ 1.5570, 0.79 g. Schlieren were evident in both fractions. There was an accidental loss of an indeterminate amount of crude product.

The product from 5.0 g. of VIII was similarly distilled: (1) b.p. 118°, $n^{25}\mathrm{D}$ 1.5540, 1.40 g.; (2) b.p. 118°, $n^{25}\mathrm{D}$ 1.5560, 1.40 g. Schlieren were evident in both fractions.

The product from 3.0 g. of crystalline 2-benzenesulfonyl-3-iodobutane was treated similarly, yielding a crystalline unsaturated sulfone, b.p. 128–132°, 0.70 g., m.p. 50–51°. Recrystallization from ethanol raised the m.p. to 51°. Calcd. for $C_{10}H_{12}SO_2$: S, 16.3. Found: S, 17.1.

Infrared spectra of the combined fractions 1 and 2 of the unsaturated sulfones from VII and VIII were identical. The absorption bands of the mixture showed all the bands observed in the spectrum of the solid isomer and several which were absent in the latter. The absorption bands found for the unrecrystallized solid isomer in CS_2 solution (1.42 g./100 ml. solution) appeared at 3.26, 3.36, 3.43, 3.52, 6.05, 7.25, 7.48, 7.60, 7.74, 8.49, 8.54, 8.80, 9.20, 9.35, 9.75, 10.00, 10.95, 11.75, 13.20, 13.75, 14.50. The new bands (*) which are attributable to the liquid unsaturated sulfone and the bands which had a larger extinction coefficient than the corresponding band in the solid isomer were detected from the spectrum of the liquid products in CS_2 (1.87 g./100 ml. solution): 3.36, 3.43, 8.00*, 8.69*, 9.20, 9.63*, 10.55*, 12.03*, 15.42*.

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[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF GULF RESEARCH & DEVELOPMENT CO., MELLON INSTITUTE, AND THE UNIVERSITY OF PITTSBURGH]

Steric and Resonance Effects in the *t*-Butyl and Isobutylphenols[1]

BY ROBERT S. BOWMAN, DONALD R. STEVENS AND W. E. BALDWIN[2]

RECEIVED MAY 25, 1956

The six mono *t*-butyl and isobutylphenols, the *t*-butyl and isobutyl phenyl ethers, *t*-butylbenzene and isobutylbenzene have been subjected to vapor phase thermal decomposition. Pronounced "*ortho*" or steric effects are observed in the *o-t*-butyl- and *o*-isobutylphenols. These effects are manifested in increased rates of dissociation and greater production of propylene when compared to the *meta* and *para* isomers. An effect attributable to phenolic resonance polarization is indicated in the *para* isomers, and is reflected by increased rates of dissociation and greater production of isobutane (from *p-t*-butylphenol) and propane (from *p*-isobutylphenol) when compared to their *meta* isomers. In general, the *m*-butylphenols resemble more closely their parent hydrocarbons, the butylbenzenes. Reaction routes are postulated in an attempt to elucidate the differences in decomposition rates and products. All of the thermal decompositions produced complex gaseous mixtures except in the case of *t*-butyl phenyl ether. In this instance, phenol and isobutylene were formed almost exclusively. Further confirmation of considerable steric interaction in the *o-t*-butyl- and isobutylphenols was afforded by (a) an investigation of the partial steric hindrance to hydrogen bonding in solution, using infrared absorption spectroscopy; and (b) a kinetic study of the rate of thermal dissociation of *o-t*-butylphenol. The rate of pressure rise in this reaction obeys first-order kinetics. The activation energy was found to be 58.4 kcal./mole.

The presence of steric strain in phenols in which one or both of the *ortho* positions are occupied by bulky alkyl substituents such as *t*-butyl groups is indicated by the ease with which the group is expelled as the olefin under the influence of various acidic reagents at 125–250°.[3] At lower temperatures in the presence of sulfuric acid the *t*-butyl group in the case of *o-t*-butylphenol has been observed to migrate to the non-hindered, stable *para* position.[4]

This present investigation was undertaken in order to study the manifestation of these "*ortho*

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[1] Abstracted from a dissertation submitted by Robert S. Bowman to the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, 1950.

[2] Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

[3] D. R. Stevens, *Ind. Eng. Chem.*, **35**, 655 (1943).

[4] H. Hart, THIS JOURNAL, **71**, 1966 (1949).