retention time as tetramethylethylene (0.65% yield). A similar run yielded no detectable tetramethylethylene.

Reactions of 2-diazopropane with zinc iodide. A. *Trace of zinc iodide.* A solution of 0.083 mole of 2-diazopropane in 400 ml. of dry ether at −25° was treated with a trace of zinc iodide, which decolorized the solution completely. The solution was washed with 1% hydrochloric acid, dried over solid potassium hydroxide, and distilled fractionally to remove excess ether. Analysis by gas chromatography showed (in addition to some acetone, most of which was lost in the earlier washing) a 36.2% yield of tetramethylethylene (based on diazo compound) and a 0.46% yield of a substance having the same retention time as 1,1,2-trimethylcyclopropane. A sample of tetramethylethylene was collected and found to have an infrared spectrum identical to that of the authentic sample prepared above, including the foreign band at 890 cm.$^{-1}$ The NMR spectrum in carbon tetrachloride showed only a single sharp signal at τ 8.4 and a few very small signals due to contaminants, which were not further investigated. It was not found possible to collect enough of the possible 1,1,2-trimethylcyclopropane for identification. No high-boiling materials were found.

Controls were run to show that neither tetramethylethylene nor 1,1,2-trimethylcyclopropane was affected by 2 hr. of refluxing in ether with equimolar amounts of zinc iodide.

B. *Excess of zinc iodide.* A solution of 0.19 mole of 2-diazopropane in 375 ml. of ether was added to 0.25 mole of zinc iodide at −35°. The immediately decolorized reaction mixture was allowed to warm to room temperature. The evolved gas (shown in four separate small runs to be about half the volume formed in the acetic acid decomposition) was shown not to contain appreciable amounts of propene by its failure to react with bromine in carbon tetrachloride (authentic propene did react) and by the absence of propene bands in the infrared spectrum. Analysis as in the preceding reaction showed the reaction mixture to contain an 11.2% yield of tetramethylethylene and a 69% yield of acetone.

C. *Excess of zinc iodide in the presence of added olefins.* An experiment essentially like the preceding except that the zinc iodide was in 100 ml. of ether saturated with propene at −60° gave a 24.4% yield of tetramethylethylene and a 1.36% yield of the substance having the retention time of 1,1,2-trimethylcyclopropane (yields based upon diazo compound). When propene was added to the reaction mixture after the reaction between zinc iodide and 2-diazopropane, the yields were 27.5% and 1.7%, respectively, of these substances.

Diphenyldiazomethane was prepared in 89–95% yields in cyclohexane by the procedure of Smith and Howard[19] from benzophenone hydrazone. The solutions of diazo compound were dried for 1 hr. over barium oxide before use.

A solution of the diazo compound in 1:1 cyclohexane-ether was decomposed with ethereal acetic acid to give a quantitative evolution of nitrogen. The reaction mixture was decolorized, washed with bicarbonate, dried, and concentrated to leave a pale yellow oil whose infrared spectrum was identical with that of an authentic sample of benzhydryl acetate.

Reaction of diphenyldiazomethane with zinc iodide. A. *Trace of zinc iodide.* To 0.075 mole of dry diphenyldiazomethane in 350 ml. of 1:1 cyclohexane–ether was added 0.001 mole of zinc iodide in 10 ml. of ether. A gas was evolved and the red solution turned yellow in a few minutes. The reaction mixture was partitioned between 1% hydrochloric acid and diethyl ether and the aqueous layer discarded. The ether layer was dried over solid potassium hydroxide and evaporated to dryness to leave 13.0 g. of a yellow solid, m.p. 160–163°. Sublimation at 180° (0.5 mm.) gave 12.5 g. (97.5% yield) of yellow crystals, m.p. 163.5–165°, which showed no depression of the mixture melting point with authentic benzophenone azine. The infrared spectrum was identical with that of an authentic sample.

Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.67; H, 5.60. Found: C, 86.69; H, 5.48.

B. *Excess zinc iodide.* To a stirred suspension of 0.2 mole of zinc iodide in 100 ml. of cyclohexane was added 0.0895 mole of diphenyldiazomethane in 250 ml. of cyclohexane over a 12-hr. period. The solution turned yellow and 0.043 mole of gas was evolved. The mixture was extracted several times with 1% hydrochloric acid, dried over solid potassium hydroxide, and evaporated to dryness *in vacuo*. Recrystallization from cyclohexane gave first 1.5 g. (10.8%) of benzophenone azine and then 14.5 g. (88.5%) of benzophenone. (In some runs these were identified by melting points and comparison of infrared spectra with authentic spectra, but where oily or impure products were obtained, the yields were determined by quantitative precipitation of benzophenone 2,4-dinitrophenylhydrazone.[20] The remaining mother liquor contained an oil which was chromatographed on alumina to give 0.17 g. (1.1%) of tetraphenylethylene, m.p. 221–223° after sublimation, mixed m.p. undepressed (lit.[21] m.p. 223–224°).

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.72; H, 6.15.

Analysis of the reaction solvent by vapor chromatography showed only a single peak with the retention time of cyclohexane. As much as 0.4% yield of cyclohexene would have been detected.

C. *Excess of zinc iodide in the presence of added olefins.* In a reaction very similar to the preceding except that the reaction medium was approximately 55% ether, 35% cyclohexane, and 10% cyclohexene, the only isolated products were benzophenone azine (19.9%) and benzophenone (74.8%). In another run, azine (60%), benzophenone (27%), and tetraphenylethylene (2.2%) were obtained. No benzhydrol was ever observed, although it was shown that the isolation procedure used would have detected 10% benzhydrol in the benzophenone.

A reaction in 55% ether, 36% cyclohexane, and 9% bicyclo[2.2.1]heptadiene gave azine (42%), benzophenone (46%), and tetraphenylethylene (8%). No products corresponding to reactions with the diene could be found, nor could benzhydrol. A second run gave 3%, 76%, and 10% yields of the three products, respectively.

Acknowledgment. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We wish also to thank the National Science Foundation and the Sloan Foundation for partial support.

Noyes Chemical Laboratory
University of Illinois
Urbana, Ill.

---

(19) L. I. Smith and K. L. Howard, *Org. Syntheses*, Coll. Vol. III, 351 (1955).

(20) R. C. Fuson, R. L. Shriner, and D. Y. Curtin, *Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, 1956, p. 219.

(21) J. E. Mackenzie, *J. Chem. Soc.*, 121, 1695 (1922).

The Stereochemistry of Ethanolysis of 2-Butyl *p*-Bromobenzenesulfonate and 2-Octyl *p*-Toluenesulfonate[1]

A. Streitwieser, Jr., and A. C. Waiss, Jr.

Received August 16, 1961

Despite the ready availability of optically active secondary alcohols, surprisingly little study has been

---

(1) Presented at the 7th Conference on Reaction Mechanisms, University of Chicago, Chicago, Ill., September, 1958.

made of the stereochemistry of solvolysis of such systems. We report the results of a study of the stereochemistry of the ethanolysis of 2-octyl *p*-toluenesulfonate and of 2-butyl *p*-bromobenzenesulfonate. Our results show that both reactions proceed with essentially complete inversion of configuration.

2-Octyl system. 2-Octanol of α_{D}^{22} +1.12°[2] with tosyl chloride and pyridine gave 2-octyl tosylate as an oil having α_{D}^{22} +0.90°. The ratio of the rotations, 0.80, is in fair agreement with that reported by Phillips,[3] 0.84. Our tosylate may have retained a small amount of solvent, but starting alcohol was shown to be absent by the infrared spectrum. Its optical purity relative to the starting alcohol was established by reaction with tetraethylammonium acetate in acetone to give 2-octyl acetate with α_{D}^{22} −0.83. This reaction should be of the direct displacement type and should give product with complete inversion of configuration. 2-Octyl acetate prepared from the alcohol with acetyl chloride and pyridine had, in two separate experiments, α_{D}^{22} +0.81°, α_{D}^{22} +0.84°, respectively. Hence, the tosylate has the same optical purity as the starting alcohol. In a similar series of experiments, Phillips[3] obtained 2-octyl acetate from the tosylate which had 93% of the optical activity of ester prepared directly from the alcohol.

The stereochemistry of ethanolysis requires also the rotation of ethyl 2-octyl ether relative to the starting tosylate, and, hence, to the starting alcohol. The most frequently used procedure has been the reaction of the potassium alcoholate with ethyl tosylate or with an ethyl halide. Although Kenyon and McNicol[4] have shown that 2-octanol can be regenerated from its potassium salt without loss of optical activity, results with this method are frequently variable[5]; for example, the ratio of the rotations of the ether and alcohol has been reported to be 1.70[4] and 1.92.[3] Mislow[6] has suggested that the reaction of an alcohol with ethyl bromide or iodide and silver oxide be used to prepare the corresponding ethyl ether without racemization. With benzyl alcohol, this method still gave some racemization,[7] but the amount was small and the method is probably more satisfactory for aliphatic alcohols. Reaction of the above 2-octanol with ethyl bromide and silver oxide gave the ethyl ether of >99% chemical purity (gas phase chromatography) and with α_{D}^{22} +2.10°; hence, the ratio relative to the alcohol is 1.88, close to the value observed by Phillips.[3] Distillation of the optically active ether from potassium resulted in partial racemization; this operation, therefore, was avoided in our study.

Solvolysis of 2-octyl tosylate was carried out in 0.2*M* solution in absolute ethanol at 50° and at 75° for about six half-lives and at 75° for about sixty half-lives. The latter experiment was run in order to determine the extent of racemization, if any, of 2-ethoxyoctane by the toluenesulfonic acid also produced by the solvolysis. The results are summarized in Table I. All of the reactions proceeded with essentially complete inversion of configuration. The product of the 50° ethanolysis had a rotation 5% higher than that of the ether prepared directly from the alcohol. The result of complete inversion is the same as that observed by Hughes, Ingold, and Masterman for the ethanolysis of 2-bromooctane.[5]

TABLE I

STEREOCHEMISTRY OF ETHANOLYSIS OF SECONDARY ALKYL SULFONATES

			Product ROC_2H_5		
Reactant	Temp.	Time (Hr.)	% purity[a]	α_{D} (corr.)[b]	% Net Inversion
2-Octyl *p*-Toluenesulfonate	50°	72[c]	100	−2.20	105[d]
	75°	15[c]	94	−2.11	100[d]
	75°	150[e]	99	−2.16	103[d]
2-Butyl *p*-bromobenzenesulfonate (A)	50°	24[c]	96	−1.200	96[f]
	25	600[c]	97	−1.245	99[f]
	25	90[c,g]	95	−1.251	100[f]
(B)	50	24[c]	99	−0.824	97[h]
	50	240[e]	99	−0.815	96[h]
	25	600[c]	99	−0.851	100[h]
	25	90[c,g]	95	−0.884	104[h]

[a] As determined by gas chromatography. Most of the samples showed a small peak due to residual pentane which was used to extract the solvolysis product. Some samples showed another peak apparently due to xylene used as a chaser in some of the distillations. [b] Actual rotations were corrected for the presence of pentane. [c] About six half-lives. [d] The rotation of ether expected for complete inversion was taken as −2.10°. [e] About sixty half-lives. [f] Rotation of ether expected for complete inversion was taken as −1.256°. [g] In 80% aqueous ethanol. [h] Rotation of ether expected for complete inversion was taken as −0.89°.

2-Butyl system. Two complete series of experiments were run with different samples of alcohol to ensure the reproducibility of the results. 2-Butyl *p*-bromobenzenesulfonate is an oil at room

---

[2] Rotations are given for 1-dc. tube unless stated otherwise.

[3] H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

[4] J. Kenyon and R. A. McNicol, *J. Chem. Soc.*, **123**, 14 (1923).

[5] E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 1196 (1937).

[6] K. Mislow, *J. Am. Chem. Soc.*, **73**, 4043 (1951).

[7] A Streitwieser, Jr., and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **81**, 4912 (1959).

temperature, but it can be purified by freezing from pentane at low temperature. However, this process results in optical fractionation; the product has a different optical purity from the starting alcohol. The relative optical purity of the brosylate in each series was determined by the displacement with tetraethylammonium acetate which has been shown to involve complete inversion of configuration in the 2-octyl case (*vide supra*). In series A, 2-butanol, α^{22}_{D} +0.66°, gave 2-butyl brosylate, $[\alpha]^{21}_{D}$ + 0.63° (still contaminated with 4% of brosyl chloride), which gave 2-butyl acetate on displacement with 94% of the optical activity of ester prepared directly from alcohol. In series B, using 2-butanol, α^{21}_{D} +0.482°, displacement of the brosylate, $[\alpha]_{D}$ +0.45°, gave ester having 82% of the optical activity of that prepared directly from the alcohol with acetyl chloride and pyridine. Optically active 2-butyl brosylate is clearly more soluble in pentane than is the racemic material.

In this series, 2-ethoxybutane was prepared by reaction of the alcohol with ethyl bromide and silver oxide. Excellent agreement was obtained for the ratio of rotation of ether to alcohol in series A and B, 2.13 and 2.16, respectively. These rotations were corrected for the fractionation observed in the preparation of the brosylate in order to arrive at the rotation of ether expected for complete inversion of configuration in the solvolyses. The results of the ethanolyses are summarized in Table I. Virtually complete inversion of configuration was again observed in all cases. The similarity of the results in ethanol at 50° for six half-lives and for sixty half-lives shows that racemization of product ether by the sulfonic acid also produced is unimportant during the solvolysis.

EXPERIMENTAL

Optical rotations were taken in wide bore tubes on a Rudolf precision polarimeter. Unless otherwise indicated, the rotations indicated are observed for 1 dc. tubes and are accurate to about ±0.01°.

(+) *2-Octyl p-toluenesulfonate.* A solution of 112.8 g. (0.866 mole) of 2-octanol, α^{22}_{D} 1.12°, in 1 l. of dry pyridine was stirred with 500 g. (2.64 moles) of *p*-toluenesulfonyl chloride in an ice bath for 2 hr. After standing overnight in the cold, the mixture was poured into ice water; the separated organic phase was washed with hydrochloric acid and with water and was dried with sodium carbonate yielding 196 g. (0.690 mole, 79.5%) of product, α^{22}_{D} + 0.895°. The infrared spectrum showed the absence of an OH band.

Displacement of 2-octyl tosylate with tetraethylammonium acetate. A solution of 11.7 g. (0.040 mole) of (+)2-octyl tosylate and 21 g. (0.156 mole) of tetraethylammonium acetate in 50 ml. of dry acetone was refluxed with stirring for 20 hr. After standing for an additional period at room temperature, the mixture was distilled at reduced pressure into a Dry Ice trap. Distillation of acetone from the distillate left a residue which was heated with 1 g. of phthalic anhydride at 110–115° overnight to remove any alcohol present. Distillation of the product gave 3 ml. of 2-octyl acetate, b.p. 78–79° (10 mm.), α^{22}_{D} −0.83°. 2-Octyl acetate prepared by the direct reaction of the alcohol, α^{22}_{D} + 1.12°, with acetyl chloride and pyridine had in two preparations, α^{22}_{D} +0.81° and α^{24}_{D} +0.84°, respectively.

(+) *2-Ethoxyoctane.* A mixture of 5.2 g. (0.04 mole) of 2-octanol (α^{22}_{D} 1.12°), 50 ml. of ethyl bromide, and excess freshly prepared dried silver oxide was refluxed for 1 week in a system protected from moisture. Excess ethyl bromide was distilled from the filtered mixture, and the residual oil was heated overnight with 0.5 g. of phthalic anhydride at 110–120°. Distillation of the product gave 2 ml. of 2-ethoxyoctane, b.p. 57–58° (10 mm.), α^{22}_{D} 2.10°. Distillation of optically active 2-ethoxyoctane from potassium resulted in partial racemization.

2-Butyl p-bromobenzenesulfonate. The reaction of the alcohol with *p*-bromobenzenesulfonyl chloride in pyridine was carried out essentially as in the 2-octyl tosylate preparation. After the reaction mixture was poured into cold dilute hydrochloric acid, the brosylate was extracted with pentane. The dried pentane extract was concentrated and cooled in a Dry Ice–acetone bath to precipitate the brosylate. After decanting the excess pentane, the ester was allowed to melt, and the remaining solvent was removed using an ice bath and a rotary evaporator. The yield of brosylate melting near room temperature averaged 57%. The 2-butanol used for batch A, α^{21}_{D} +0.626°, gave brosylate, $[\alpha]^{21}_{D}$ +0.63 ± .01° (*c* 16, acetone). In batch B, alcohol, α^{21}_{D} +0.482°, gave brosylate, $[\alpha]^{21}_{D}$ +0.45 ± .02° (*c* 16, acetone). This brosylate gave a good analysis.

Anal. Calcd. for $C_{10}H_{13}O_3SBr$: C, 40.96; H, 4.47; S, 10.94; Br, 27.26. Found: C, 40.84; H, 4.39; S, 10.85; Br, 27.32.

Displacement of 2-butyl p-bromobenzenesulfonate with tetraethylammonium acetate. The reaction of 2-butyl *p*-bromobenzenesulfonate with tetraethylammonium acetate in acetone was carried out essentially as in the case of 2-octyl tosylate. The brosylate, batch A, gave 2-butyl acetate, α^{22}_{D} −1.12°. Reaction of the alcohol used in this batch directly with acetyl chloride and pyridine gave 2-butyl acetate, α^{22}_{D} +1.22°. The displacement with batch B gave acetate, α^{22}_{D} −0.78°; acetate prepared from the alcohol with acetyl chloride and pyridine had α^{22}_{D} +0.945°. In each case, the purity of the product esters was determined by gas chromatography.

2-Ethoxybutane. The ethers were prepared by reaction of the alcohol with ethyl bromide and silver oxide essentially as in the case of 2-ethoxyoctane. 2-Butanol used for batch A gave ether, α^{26}_{D} 1.30°; ether from batch B had α^{22}_{D} +0.99°. Gas phase chromatography of the products showed the presence of a total of about 4% of other components which were probably pentane, xylene (used as a chaser in the distillations), and a trace of starting alcohol.

Solvolyses. The solvolyses were run by dissolving 0.04 mole of sulfonate ester in 200 ml. of solvent which had been preheated in a thermostat at the appropriate temperature. The solution was maintained at the desired temperature for the indicated time and was then diluted with ice water and extracted with pentane. The washed and dried pentane extract was distilled to remove the solvent. The residue was treated with phthalic anhydride and was distilled through a small column. In the butyl cases, xylene was usually used as a chaser. The yields ranged between 1 and 2 ml. of product ether on which the rotation was taken. Gas phase chromatography usually indicated the presence of a few percent of other components undoubtedly pentane and xylene. The observed rotations were corrected for the presence of these other components which were taken to be optically inactive.

From the solvolyses of 2-butyl brosylate in 80% aqueous ethanol, only the ether was isolated.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIF.