anol, 2.5–3.0 g. (33–40%), m.p. 247–249° (sealed), neut. equiv. 289.

Anal. Calcd. for $C_{15}H_{19}O_3N_3$: N, 14.52. Found: N, 14.54.

Resolution of the 4-(4-Carboxyphenyl)-semicarbazone of *dl*-3-Methylcyclohexanone.—A mixture of 1400 ml. of methanol and 17.7 g. (0.06 mole) of the 4-(4-carboxyphenyl)-semicarbazone of *dl*-3-methylcyclohexanone was brought to boil and 26.6 g. (0.06 mole) of brucine,[8] dissolved in a small amount of methanol, was added. Solution of the derivative occurred immediately; the volume was reduced to 1100 ml. and allowed to stand overnight on a slowly cooling steam-bath. Any crystalline formation was redissolved by heating, the solution filtered hot, reduced to 1000 ml. and cooled slowly in an oven constant at 30°. The fine yellow crystals thus obtained were recrystallized three times from methanol at a solvent ratio of 22–25 ml./g. of salt and using a second crop from the previous recrystallization added to the following mother liquor.[9] The optically pure product, as golden rosettes, decomposed erratically when melted. The yield was 10.1 g. (24%), $[\alpha]^{20}\mathrm{D}$ −22.2° (*c* 0.397 chloroform, 1 dm.).

Anal. Calcd. for $C_{38}H_{45}O_7N_5$: N, 10.27. Found: N, 10.19.

Slurrying 2.0 g. of the salt in 20 ml. of water, acidifying with 2 ml. of glacial acetic acid, collecting and drying gave quantitative recovery of the derivative, neut. equiv. 290.

Refluxing of 9.7 g. of the pure salt for 10 minutes with 19 ml. of 9 *N* sulfuric acid, cooling, extracting with ether, drying and removing the ether, left a residual oil, b.p. 167–169°, $n^{20}\mathrm{D}$ 1.4444 (Adams, Smith and Loewe[10] report b.p. 164–168°, $n^{20}\mathrm{D}$ 1.4449), which was converted to the semicarbazone in the usual manner. After one recrystallization from methanol, this semicarbazone of *l*-3-methylcyclohexanone melted at 183°, $[\alpha]^{20}\mathrm{D}$ + 20.6° (*c* 1.159 absolute ethanol, 1 dm.); Leonard and Boyer[3] reported m.p. 179–180°, $[\alpha]^{20}\mathrm{D}$ +20.6°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Stereochemistry of the Primary Carbon. IX. Solvolysis of Optically Active 1-Butyl-1-*d* *p*-Nitrobenzenesulfonate in Dibutyl Ether–Acetic Acid[1-3]

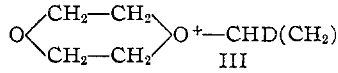
BY A. STREITWIESER, JR., AND S. ANDREADES[4]

RECEIVED AUGUST 8, 1958

The acetolysis of optically active 1-butyl-1-*d* *p*-nitrobenzenesulfonate in 55% dibutyl ether–45% acetic acid (by volume) produces 71% of 1-butyl-1-*d* acetate with 97 ± 6% net inversion of configuration and 29% of undeuterated butyl acetate. The latter product presumably arises via a through a tributyloxonium ion intermediate. Under the reaction conditions 38% of the total product resulted from cleavage of the dibutyl ether by the *p*-nitrobenzenesulfonic acid produced in the solvolysis.

It has been previously demonstrated[5] that the solvolysis in acetic acid of optically active 1-butyl-1-*d* *p*-nitrobenzenesulfonate (I-*d*) proceeds with 85% inversion of configuration and 15% racemization. The significant amount of racemization which resulted was taken as evidence for the formation to some extent of symmetrically solvated primary carbonium ions (II, $S_1 = S_2$ = AcOH) in this system. The increased racemization found to result from the presence of dioxane or nitrobenzene was associated with the formation of carbonium ion intermediates (II) at least partially solvated by the addend solvent. The existence of II ($S_1 \neq S_2$) was inferred by analogy with the II ($S_1 = S_2$) presumed to account for the racemization in pure AcOH.[6] The possible formation of intermediates such as the oxonium salt III in the dioxane case was recognized but was not determined. The formation and subsequent acetolysis of such intermediates in the mixed solvent would surely result in greater net racemization. Trialkyloxonium salts have been isolated and are known to be rather reactive.[7] Despite the many kinetic studies of solvolyses of various systems in solvents containing ethers, particularly dioxane, the possible role of such oxonium salts as intermediates never has been evaluated. Alkoxy groups have been shown in many cases to provide neighboring group participation with the formation of cyclic oxonium ion intermediates[8]; these reactions, however, are intramolecular and involve a more favorable entropy change. In this paper we report experiments using deuterium simultaneously as an isotopic tracer and as a source of optical asymmetry which relate to the role of intermolecular oxonium ion formation in solvolysis reactions.

II



III

Results and Discussion.—1-Butanol-1-*d* having $\alpha^{25}\mathrm{D} + 0.119 \pm 0.008°$ (*l*4) was converted with acetyl chloride and pyridine to the acetate which had $\alpha^{25}\mathrm{D} - 0.167 \pm 0.003°$ (*l*2). The ratio of the rotations agrees within experimental error with values previously reported.[5] When the corresponding *p*-nitrobenzenesulfonate was solvolyzed in 55% dibutyl ether–45% acetic acid (by volume) for 5.5 half-lives at 100° the product acetate had $\alpha^{25}\mathrm{D} + 0.071 \pm 0.003°$ (*l*2), which corresponds to 42.5 ± 2.5% apparent net inversion (57.5 ± 2.5% racemization), but this product had lost 56 ± 1% of its deuterium. Hence, the 1-butyl-1-*d* acetate (IV-*d*)

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(1) This paper was taken in part from the Ph.D. thesis of S. Andreades, University of California, 1958.

(2) Presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 16, 1958.

(3) 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 this fund.

(4) National Science Foundation Predoctoral Fellow, 1957–1958.

(5) A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **79**, 6233 (1957).

(6) See also E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1201 (1937); and A. Streitwieser, Jr., *Chem. Revs.*, **56**, 655 (1956).

(7) H. Meerwein, *et al.*, *J. prakt. Chem.*, **147**, 257 (1937); **154**, 83 (1939); *Ber.*, **89**, 2060 (1956).

(8) S. Winstein and R. B. Henderson, THIS JOURNAL, **65**, 2196 (1943); S. Winstein, C. R. Lindegren and L. I. Ingraham, *ibid.*, **75**, 147 (1953); D. S. Noyce and B. R. Thomas, *ibid.*, **79**, 755 (1957); S. Winstein, E. Allred, R. Heck and R. Glick, *Tetrahedron*, **3**, 1 (1958).

present was actually formed with 97 ± 6% inversion of configuration but is diluted with undeuterated butyl acetate (IV) also formed during the solvolysis.

$$(CH_3CH_2CH_2CH_2)_2O^+CHDCH_2CH_2CH_3$$

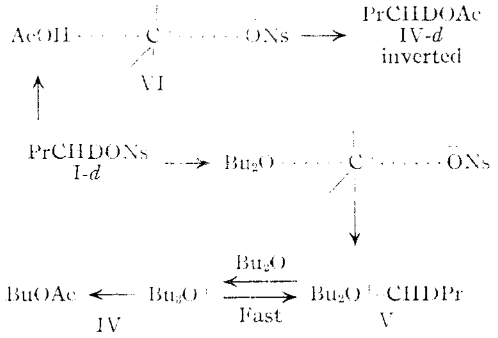
V

Dibutyl ether was chosen as one component of the solvent mixture because the corresponding oxonium ion V, if formed as an intermediate, would result in at least partial reaction at the undeuterated butyl groups and give rise to loss of deuterium in the product. A corresponding reaction at a methylene group in the dioxane moiety of III is not expected because of the deactivating effect of β-oxygens. In previous acetolyses of I-*d* the product IV-*d* was demonstrated to be optically stable to the reaction conditions; by analogy, product stability is assumed in the present case. However, the *p*-nitrobenzenesulfonic acid also formed in the solvolysis could conceivably cleave dibutyl ether with subsequent formation of undeuterated butyl acetate. Indeed, when a solution of *p*-toluenesulfonic acid in dibutyl ether–acetic acid was maintained under the solvolysis conditions, a significant amount of butyl acetate was formed. The amount of ether cleavage which actually occurred during the acetolysis experiment was determined by repeating the solvolysis with *n*-butyl *p*-nitrobenzenesulfonate (I) and using an isotopic dilution technique to obtain the total yield of butyl acetate. At the end of the reaction, a known amount of 1-butyl-1,1-d_2 acetate was added to the mixture. The deuterium analysis of the butyl acetate isolated from the mixture showed that the yield of ester from the reaction was 161 ± 8%. If all of the undeuterated butyl acetate produced during the first solvolysis had come from ether cleavage, the total yield of ester in the isotopic dilution experiment would have been 226%. This argument implies that the acetolysis of the primary sulfonate is stoichiometric. No significant amounts of olefin from elimination were ever detected in our solvolyses; the solvolyses were carried out in sealed vessels and no pressure increase was noted on opening. Furthermore, under these sealed conditions in acid media further solvolysis of any 1-butene formed would be expected and would yield *sec*-butyl acetate. No *sec*-butyl acetate ever was observed in our acetolyses. Huisgen and Rüchardt[9] have reported that under more vigorous conditions (310 hours at 120°) the acetolysis of *n*-propyl tosylate yields less than 3% of isopropyl acetate.

We conclude that in the first solvolysis 38 ± 3% of the product acetate resulted from ether cleavage; of the 62 ± 3% which resulted from the sulfonate solvolysis itself, 71 ± 4% was formed without loss of deuterium and with 97 ± 6% net inversion of configuration and 29 ± 4% was formed with loss of deuterium. The last material could reasonably have arisen only from the intervention of V as a discrete but unstable intermediate. The optical result demonstrates further that relatively little of the oxonium ion V formed could actually have reacted directly with acetic acid for deuterated and retained or racemized acetate would result and we are limited to only 3 ± 6% of such racemization.

The ratio of deuterated to undeuterated butyl acetate produced by solvolysis of I-*d* (2.5 ± 0.5) is the same as the molar ratio of acetic acid to dibutyl ether in the solvent (2.4); toward I, dibutyl ether and acetic acid have about the same effective nucleophilicities. If this equality also held toward V and if the formation of V and its reaction with acetic acid both proceeded with essentially complete inversion of configuration, about 7% of the reaction would have proceeded to give IV-*d* with retention; or, the IV-*d* formed would have been about 20% racemized. Thus, the reaction of V with dibutyl ether to give virtually complete effective exchange of deuterium with solvent must be considerably faster than the reaction with acetic acid. The results are consistent with the over-all reaction sequence outlined in Chart I in which only the important reactions are given. The optical results also demonstrate that the presence of an ether also decreases the formation of II ($S_1 = S_2 = AcOH$) from VI.

Chart I



This demonstration that oxonium ion intermediates are important in this solvolysis indicates that the interpretation of kinetic and other data in ether solvents must consider not only solvation effects but also the possible formation of discrete oxonium salt intermediates.

The solvolysis of I in 55% diethyl ether–45% acetic acid produced a mixture containing butyl acetate, ethyl acetate, ethyl butyl ether and small amounts of ethanol and butanol; however, when *p*-nitrobenzenesulfonic acid was heated in this solvent mixture, ethyl acetate, ethanol and ethyl *p*-nitrobenzenesulfonate were formed. No further attempt was made in this system to distinguish ether cleavage from solvolysis products.

In the presence of a cyclic oxide which can open, it was thought that polymeric products could be obtained. Prolonged maintenance of I in tetrahydrofuran at 100° liberated acid and produced black tars which were not investigated further.

Experimental

All infrared spectra were carried out on a Baird double-beam recording infrared spectrophotometer, with sodium chloride optics.

Optically Active 1-Butanol-1-*d*.—The synthetic sequence used in this work was essentially the same as that published previously[5] with some modifications which are included below. The reduction of (+)-camphor with lithium aluminum deuteride gave a quantitative yield of the deuterated iso-

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[9] R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1 (1956).

borneol–borneol mixture[10] which was uncontaminated with camphor as shown by the absence of any carbonyl absorption in the infrared, and which had $[\alpha]^{28.5}$D $-22.38 \pm 0.16°$ (*c* 25, benzene).

The asymmetric reduction was carried out using isobornyloxy-2-*d*-magnesium bromide as before, but the reaction mixture was not cooled prior to the addition of *n*-butyraldehyde. The resulting higher temperature resulted in less stereospecificity. Consequently, after purification of the deuterioalcohol *via* recrystallization of the hydrogen phthalate to constant rotation and subsequent regeneration, 1-butanol-1-*d* was obtained which had α^{25}D $+0.088 \pm 0.003°$ (*l* 2) and 0.50 deuterium atom per molecule as indicated by infrared comparison with a standard sample of inactive 1-butanol-1-*d* prepared by reduction of butyraldehyde with lithium aluminum deuteride. This rotation is only about 57% of the magnitude of rotation produced previously.[5] The optically active 1-butanol-1-*d* thus produced was diluted with inactive 1-butanol-1-*d* to give material with α^{25}D $+0.119 \pm 0.008°$ (*l* 4) and which contained 0.65 deuterium atom per molecule (infrared).

The optical dispersion from 650 to 400 mμ of this material will be published separately.[11]

1-Butyl-1-*d* Acetate (IV-*d*).—Diluted 1-butanol-1-*d*, α^{25}D $+0.119 \pm 0.008°$ (*l* 4), was converted to the corresponding acetate with acetyl chloride and pyridine.[5] The acetate had α^{25}D $-0.167 \pm 0.003°$ (*l* 2).

Solubility Determinations of *p*-Nitrobenzenesulfonic Acid in Di-*n*-butyl Ether–Acetic Acid Mixtures.—Various solvent mixtures of dibutyl ether and acetic acid were made up by mixing the parts by volume indicated below. An excess of *p*-nitrobenzenesulfonic acid was shaken with each of the solvent mixtures so that a considerable amount of undissolved solid phase was present to equilibrate with the liquid phase. The samples were stoppered and allowed to equilibrate overnight. (Although this may not have been long enough for complete equilibration, the values so obtained would be *minimum* solubilities which would be completely satisfactory for our purposes.) The solutions were then shaken and filtered. A 1-cc. aliquot of each filtrate was titrated potentiometrically in acetic acid using a model G Beckman *p*H meter and calomel and glass electrodes. A standardized solution of sodium acetate in acetic acid was used as titrant. The results which follow are given as volume per cent. dibutyl ether in the solvent mixture and solubility of *p*-nitrobenzenesulfonic acid in moles per liter: 75%, 0.037; 60%, 0.153; 55%, 0.203; 50%, 0.402.

1-Butyl *p*-Nitrobenzenesulfonate (I).—The procedure described previously[5] gave a 90% yield of product, m.p. 62–63°.

Anal.[12] Calcd. for $C_{10}H_{13}O_5NS$: C, 46.32; H, 5.05. Found: C, 46.66; H, 5.11.

1-Butyl-1-*d* *p*-Nitrobenzenesulfonate (I-*d*).—The procedure was repeated using 1-butanol-1-*d*, α^{25}D $+0.119°$ (*l* 4). After recrystallization from benzene–hexane, the product had m.p. 62.8–63.2° (Fisher–Johns melting point apparatus, using a very slow temperature increase).

Anal.[12] Calcd. for $C_{10}H_{12}DO_5NS$: C, 46.14; H + D, 5.42. Found: C, 45.90; H + D, 5.23.

Kinetics of Acetolysis of 1-Butyl *p*-Nitrobenzenesulfonate in 55% Dibutyl Ether–45% Acetic Acid at 100°.—The dibutyl ether used throughout this work was distilled through a 16-plate Oldershaw column and material boiling in the range 141–142° was collected. Glacial acetic acid (Mallinckrodt analytical reagent) was analyzed for water,[12] an equivalent amount of acetic anhydride was added and the mixture was refluxed for about one hour.

A mixture of 27.5 ml. of dibutyl ether and 22.5 ml. of acetic acid was used to dilute 1.2895 g. of I to 25 ml. in a volumetric flask maintained at 20°. The resulting solution was 0.199 *M*. Aliquots of this solution were sealed in glass vials and immersed in a constant temperature flask which was filled with white oil and maintained at 100° by refluxing distilled water. One vial was retained for the initial titer. The solutions darkened with time probably at least in part because of decomposition of the sulfonic acid liberated; the experimental infinity titer was about 10% lower than the calculated infinity titer. Titrations were carried out potentiometrically as described under solubility determinations. The equation for a first-order reaction was used, using the calculated infinity titer.

TABLE I

KINETICS OF ACETOLYSIS OF 1-BUTYL *p*-NITROBENZENESULFONATE IN 55% DI-*n*-BUTYL ETHER–45% ACETIC ACID AT 100°

Time, sec.	Titer	Reaction, %	$10^5 k$, sec.$^{-1}$
0	0	0	
10,800	0.53	14.86	1.49
18,960	0.863	24 20	1.46
32,400	1.39	38.98	1.53
39 600	1.569	44.00	1.47
79,200	2.390	67.02	1.40
∞	3.566 (calcd.)	Av.	1.47 ± 0.03

Solvolysis of Optically Active 1-Butyl-1-*d* *p*-Nitrobenzenesulfonate in 55% Dibutyl Ether–45% Acetic Acid at 100°.—In 485 ml. of a solution prepared by mixing 275 ml. of dibutyl ether and 225 ml. of acetic acid was dissolved 25.0 g. (0.096 mole) of optically active 1-butyl-1-*d* *p*-nitrobenzenesulfonate. The reaction mixture was maintained at 100° for 72.5 hours (5.5 half-lives) in a constant temperature flask (stoppered) using refluxing distilled water. The solution darkened to an amber color. After cooling to 0° in an ice-bath, the reaction mixture was brought to about *p*H 10 by the slow addition of 1 l. of ice-water containing 160 g. (4 moles) of dissolved sodium hydroxide. The aqueous layer was separated and extracted four times with 100-ml. portions of pentane. The combined organic layers were dried with anhydrous sodium sulfate. A small amount of black polymeric material was separated with the aqueous extracts. After removal of most of the pentane through a two-foot Vigreux column, the residue was distilled through a one-foot glass spiral column, collecting: fraction A, b. p. 103 – 133.5°, 25 cc.; fraction B, b. p. 133.5–134°, 20 cc.; and fraction C, b. p. 134–137°, 25 cc. The residue was distilled through a 16-plate Oldershaw column to give fraction D, b. p. up to 141.5°, 30 cc.; and fraction E, b. p. 141.5°, 25 cc. leaving a residue of about 100 cc. Fraction E was shown to be pure dibutyl ether by comparison of its infrared spectrum with that of an authentic sample.

Fraction A was refractionated through a two-foot tantalum-wire-coil column similar to that described by Mitchell and O'Gorman[13] which was rated at 35 plates under total reflux. Six fractions were collected. From infrared spectra of all fractions and of known mixtures, it was shown that fraction 1 was largely pentane; fraction 2, 0.8 ml., was largely butanol; fraction 3, 2.8 ml., was about 10% butanol, 90% *n*-butyl acetate (estimated from the O–H absorption at 2.9μ); fractions 4 and 5 were essentially pure *n*-butyl acetate. Using known mixtures of *n*-butyl acetate and dibutyl ether, it was shown that as little as 1% of dibutyl ether in butyl acetate could be detected because of the extremely intense absorption by the ether at 9μ. Hence, fractions 4 and 5 (*ca.* 3.6 ml.) were >99% butyl acetate (containing deuterium). Fraction 6, 1.0 ml., was largely ether. The fact that pure butyl acetate could be obtained from such a mixture using this column was previously demonstrated in a dry run.

Fractions 4 and 5 were combined and the optical dispersion was determined[11]; α^{25}D $+0.071 \pm 0.003°$ (*l* 2). By comparison with the rotation of the 1-butyl-1-*d* acetate prepared above, the solvolysis product shows 42.5 ± 2.5% apparent net inversion and 57.5 ±2.5% racemization.

The solvolysis product was analyzed for deuterium in the infrared by comparing the C–D stretching band in the 2200 cm.$^{-1}$ region with that of known mixtures of the standard IV-*d* and IV. The results showed that 55.7 ± 1% of the deuterium originally present was effectively lost during the solvolysis.

Control Run to Test for Cleavage of Dibutyl Ether.—An approximately 0.2 *M* solution was prepared by dissolving 18.7 g. (0.096 mole) of *p*-toluenesulfonic acid monohydrate in a mixture of 225 ml. of acetic acid, 275 ml. of dibutyl ether

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[10] D. S. Noyce and D. S. Denney, THIS JOURNAL, **72**, 5743 (1950).

[11] I. Tinoco, S. Andreades and A. Streitwieser, Jr., (forthcoming).

[12] Analysis by the Microanalytical Laboratory, Department of Chemistry, University of California.

[13] F. W. Mitchell, Jr., and J. M. O'Gorman, *Anal. Chem.*, **20**, 315 (1948).

and 12.5 g. (0.122 mole) of acetic anhydride. The reaction mixture was sealed and heated to 100° in the constant temperature flask with refluxing distilled water for 72 hours. The mixture was processed in the same manner as was the solvolysis mixture; final distillation through the Oldershaw column yielded fraction 1, b. p. 39–130°, 3 ml.; fraction 2, b. p. 130–135°, 1.5 ml.; and fraction 3, b. p. 135–140°, 13.0 ml. The infrared spectra showed the presence of butyl acetate in all three fractions. The fractions were combined and a weighed sample was diluted with a weighed sample of spectro grade carbon tetrachloride. The infrared spectrum was taken in a 0.121-mm. cell using a 0.118-mm. cell containing pure carbon tetrachloride as the reference. Authentic mixtures of dibutyl ether and butyl acetate were prepared, brought to the same dilution with carbon tetrachloride and the infrared spectra were taken in the same cells. In this manner, it was estimated that approximately 2.3 ml. (2.0 g.) of butyl acetate was formed. No alcohol band was apparent.

Isotopic Dilution Experiment for Determination of Excess *n*-Butyl Acetate Produced in the Solvolysis.—In a constant temperature flask, 220 ml. of dibutyl ether was added to 20.0 g. (0.0771 mole) of I dissolved in 180 ml. of dry acetic acid. A neoprene stopper was wired on and the solvolysis was carried out under conditions identical to the previous solvolysis of I-*d*. Before processing the reaction mixture, however, 4.0835 g. of 1-butyl-1,1-d_2 acetate was added. The same procedure was used as before checking carefully for purity of the product with infrared techniques.

The butyl acetate fraction was analyzed for deuterium in the infrared using the analytical curve technique with standard mixtures. Since the ester contained 22.0 ±0.8% of 1-butyl-1,1-d_2 acetate, 14.5 ± 0.7 g. of butyl acetate was produced in the solvolysis. The theoretical yield is 8.96 g.; hence the yield is 162 ±8%.

Test for Solvolytic Cleavage of Diethyl Ether.—In 450 ml. of a mixture of 55% (by volume) of anhydrous diethyl ether and 45% of acetic acid was dissolved 23.5 g. (0.091 mole) of I to give an approximately 0.2 *M* solution. The reaction mixture was heated to 100° for 72 hours in a constant temperature flask using refluxing distilled water as the heating bath. After cooling and basification with aqueous sodium hydroxide in the usual manner, the aqueous layers were extracted with ether. The ether extracts were dried and distilled. A series of fractions were obtained which were shown to consist of ethanol, ethyl acetate, 1-butanol, *n*-butyl acetate and very probably *n*-butyl ethyl ether. The analysis was carried out by infrared spectroscopic comparison with authentic mixtures and by gas phase chromatographic analysis of the products and of authentic mixtures using a K and M Scientific Glassware Co. model 17A gas phase chromatograph. The column was packed with a 25% liquid partition of Dow–Corning Silicone grease on Celite (35/80 mesh, Johns–Manville Chromasorb). The chromatography was conducted at room temperature using helium flow rates of about 50 ml./min. and a filament current of 400 ma. A Varian Recorder, model G10, was used in conjunction with the instrument.

Control Run to Test for Cleavage of Diethyl Ether by *p*-Nitrobenzenesulfonic Acid.—Enough acetic anhydride was added to a 0.2 *M* solution of *p*-nitrobenzenesulfonic acid hydrate in 55% (by volume) anhydrous diethyl ether, 45% acetic acid to take up the calculated amount of water in the sulfonic acid. The reaction was conducted under the same conditions as the previous experiment and was processed in the same manner. Ethyl acetate was identified by comparison of its infrared spectrum with that of an authentic sample. Distillation yielded approximately 5 cc. which was contaminated with ethanol. A pure cut was obtained for the infrared comparison. From the residues, crystalline ethyl *p*-nitrobenzenesulfonate was isolated, m.p. 91.5–92.5° (lit.[14] m. p. 92–92.5°).

Anal.[12] Calcd. for $C_8H_9O_5NS$: C, 41.55; H, 3.92; N, 6.06. Found: C, 41.85; H, 3.96; N, 6.14.

Treatment of *n*-Butyl *p*-Nitrobenzenesulfonate with Tetrahydrofuran at 100°.—Commercial tetrahydrofuran was purified by refluxing 10 liters for 6 hours with 1.5 lb. of phosphorus pentoxide. The mixture was distilled and 7 liters (b. p. 65–66°) was collected. The distillate was distilled from sodium ribbon before use.

A solution of 10 g. of I in 130 ml. of tetrahydrofuran was maintained at 100° for 13 days in a constant temperature flask. After cooling, the reaction mixture was found to be acidic. The mixture was brought to about *p*H 7 by the addition of dilute sodium hydroxide solution. After removal of most of the tetrahydrofuran by distillation, 200 ml. of salt water was added and the aqueous solution was extracted 3 times with 100-ml. portions of ether. The combined ether extracts were dried with anhydrous sodium sulfate and the ether was evaporated. Only a black viscous liquid and carbonaceous material remained. Most of this residue was dissolved in hot benzene, but fractional additions of hexane caused only the separation of black tars. No tractable products could be obtained.

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[14] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo Compounds.[1] Decomposition of Large Ring Azo Compounds

BY C. G. OVERBERGER, I. TASHLICK,[2a] M. BERNSTEIN[2b] AND R. G. HISKEY

RECEIVED JUNE 20, 1958

The rates of decomposition of the cyclic azo compounds (II, n = 6, 8, 10) have been determined at three temperatures. All three compounds were found to have activation energies for the decomposition and spectral properties similar to a linear analog, 1-azo-bis-1-phenylpropane. The decomposition of II, n = 8, in *cis*-stilbene yielded only a trace of adduct, while *cis*-stilbene scavenged 16% of the radicals from 1-azo-bis-1-phenylpropane, demonstrating a cage effect operating in the case of the diradicals produced.

In a continuation[3] of a study concerned with the preparation and properties of moderately active diradicals in solution[3] (A discussion of organic diradicals and their role in polymerization appears in reference 3), the results obtained with the 24-membered ring azo compound (II, n = 8), previously reported,[3] are compared with several other large ring azo compounds. This paper describes the preparation of 20-, 24- and 28-membered ring azo compounds (II, n = 6, 8, 10), the spectral properties of the corresponding azines and azo compounds, the determination of the rates of decomposition of the azo compounds at three temperatures and the decomposition of the 2,4-mem-

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[1] This is the 26th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger and I. Tashlick, THIS JOURNAL, in press.

[2] (a) This paper comprises a portion of a thesis presented by Mr. I. Tashlick in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn. (b) This paper comprises a portion of a thesis presented by Mr. M. Bernstein in partial fulfillment of the requirements for the Bachelor of Science degree in the Polytechnic Institute of Brooklyn.

[3] C. G. Overberger and M. Lapkin, THIS JOURNAL, **77**, 4651 (1955).