in carbon tetrachloride and chromatographed on a neutral alumina column. No IV was eluted with either petroleum ether (b.p. 60–70°) or cyclohexane. However, elution with a 50:50 carbon tetrachloride–benzene mixture gave 0.20 g. of solid, m.p. 300–310°. Recrystallization from a large volume of cyclohexane gave 0.15 g. (7.5%) of dimer III, m.p. 310–313° (m.m.p.).

Reaction of I with Maleic Anhydride. a. In Refluxing Carbon Tetrachloride (Attempted).—A solution of 1.0 g. (3.67 mmoles) of I and 0.36 g. (3.67 mmoles) of maleic anhydride in 25 ml. of carbon tetrachloride was refluxed for 48 hr. Evaporation of the solvent gave a semisolid mass. Addition of petroleum ether (b.p. 28–38°) gave 0.88 g. of recovered I, m.p. and m.m.p. 74–76° (88%).

b. **In a Sealed Tube at *ca.* 150°.**—One gram (3.67 mmoles) of I and 0.36 g. (3.67 mmoles) of maleic anhydride was heated in a sealed tube at 150–160° (0.5 mm.) for 3 hr. The resulting solid pellet was dissolved in hot benzene and chromatographed on an acidic alumina column. Elution of the column gave only a glass-like polymeric material which could not be induced to crystallize.

Reaction of I with Dimethyl Acetylenedicarboxylate (Attempted).—One gram (3.67 mmoles) of I and 1.0 g. (7.1 mmoles) of dimethyl acetylenedicarboxylate were heated at 100–110° (under a nitrogen atmosphere) for 18 hr. Cooling gave a yellow oil which resisted crystallization attempts. This oil was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on an acidic alumina column. Elution with the same solvent gave 0.8 g. (80%) of recovered I, m.p. and m.m.p. 73–75°. Further elution gave only small amounts of yellow oil.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

Olefinic Cyclizations. VI. Formolysis of Some Branched-Chain Alkenyl *p*-Nitrobenzenesulfonates[1]

BY WILLIAM S. JOHNSON AND RAYMOND OWYANG

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Formolysis of 5-methyl-5-hexenyl *p*-nitrobenzenesulfonate gave cyclized material in only 39% yield. The remainder of the product consisted mainly of compounds arising from attack by formic acid on the terminal olefinic bond of the substrate. The main course of the formolysis of 4-methyl-4-pentenyl *p*-nitrobenzenesulfonate involved rearrangement to the 4-methyl-3-pentenyl ester, followed by solvolysis of the homoallylic system. The formolysis of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate (I) at 75° proceeded about 20 times as fast as that of the *n*-hexyl ester. The products were mainly those of five-membered ring closure, namely substances II, III, IV, and V. In addition, 2,2-dimethylcyclohexanol (VI) was identified among the products. This last substance was formed in increasing amounts, at the expense of the five-membered ring products, as the reaction period was lengthened. 6-Methyl-6-heptenyl *p*-nitrobenzenesulfonate, on formolysis, gave essentially the same products as the 6-methyl-5-heptenyl ester, indicating an isomerization of the former to the latter prior to solvolysis. A trace of 1-methylcycloheptanol was produced.

In a previous study[2] we examined the formolysis of 4-pentenyl, 5-hexenyl, and 6-heptenyl *p*-nitrobenzenesulfonate. The present study was undertaken with the view to determining how methyl substituents on the olefinic bonds would affect the rate and course of the reaction.

The 5-Methyl-5-hexenyl System.—The solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate at 75° in formic acid containing sodium formate has been shown[2] to proceed at a rate which is about twice that of the solvolysis of the hexyl ester. The participation of the olefinic bond in the formolysis was attended by production of cyclized material in over 70% yield. It was considered of interest to examine the formolysis of the 5-methyl-5-hexenyl ester which, because of the more reactive olefinic bond, was expected to proceed with even larger rate acceleration to give higher yields of cyclized products than in the case of the 5-hexenyl ester. 5-Methyl-5-hexenyl *p*-nitrobenzenesulfonate, m.p. 43–45°, was prepared from the known alcohol. After treatment with formic acid–sodium formate for 2 hr. at 75°, the solvolysis was only 65% complete, indicating a rate comparable to that obtained with the saturated hexyl ester (63% completed under the same conditions). That there was relatively little participation of the olefinic bond was confirmed by the low yields of cyclic material which was identified (after ester cleavage) as 1-methylcyclohexanol (29% yield) and 1-methylcyclohexene (10% yield). The explanation of the failure of this relatively reactive olefinic bond to participate as much as expected in the solvolysis was forthcoming from examination of the remainder of the solvolysis product which proved to be a mixture of 5-methyl-1,5-hexanediol (10% yield) and 5-methyl-4-hexenol (16% yield). (An authentic specimen of the diol, with a bis-*p*-nitrobenzoate melting at 130–131°, was prepared by treating 5-methyl-5-hexenol with formic acid, followed by cleavage of the formates with lithium aluminum hydride.) These two solvolysis products must have arisen from a rapid competing process involving attack by formic acid on the terminal olefinic bond of the substrate to produce 5-formyloxy-5-methylhexyl *p*-nitrobenzenesulfonate by an addition process, and 5-methyl-4-hexenyl *p*-nitrobenzenesulfonate by a proton abstraction process. These two modified *p*-nitrobenzenesulfonates would be expected to undergo solvolysis at rates comparable to, or slower than, that of the saturated ester to give, by direct displacement, the observed products. The 35% of unsolvolyzed material in the experiment described above must have consisted largely of these two *p*-nitrobenzenesulfonates.

(1) Part V of this series: W. S. Johnson and J. K. Crandall, *J. Am. Chem. Soc.*, **86**, 2085 (1964).

(2) W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *ibid.*, **86**, 1959 (1964).

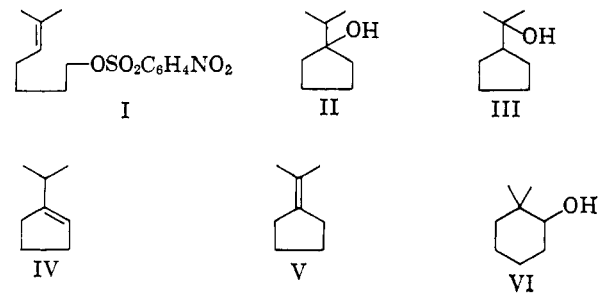
It is to be expected that solvolysis of the 5-methyl-5-hexenyl ester in a less acidic medium, which will not attack the terminal olefinic bond so rapidly, will result in rate acceleration and higher yields of cyclization.[3] An attempt to minimize the competing attack of the olefinic bond through an increase in the amount of sodium formate from 2 to 50 mole equivalents served only to increase the ratio of 1-methylcyclohexene (20% yield) to 1-methylcyclohexanol (20% yield).

The 4-Methyl-4-pentenyl System.—An examination of the formolysis of 4-methyl-4-pentenyl *p*-nitrobenzenesulfonate, m.p. 43.5–45°, was undertaken as a comparison with the 4-pentenyl ester because solvolysis of the latter was known[2] to give only the product of direct substitution, there being no detectable amount of cyclic product. It was considered of interest to determine if the additional methyl group, which would afford the opportunity of generation of cyclic tertiary instead of secondary cation, would promote five-membered ring closure. The formolysis of the methylpentenyl ester was 50% complete in 30 min. at 75°, whereas the pentenyl ester required 90 min. This rate acceleration, however, was not caused by participation of the 4,5-double bond to give cyclization, since 1-methylcyclopentanol was produced in only about 1% yield. The rate enhancement evidently was the result of bond migration of the type described above to give 4-methyl-3-pentenyl *p*-nitrobenzenesulfonate which, being a homoallylic system, undergoes solvolysis with rate enhancement.[4] This conclusion follows from the identification, among the solvolysis products, of 4-methyl-3-pentenol. In a formolysis which was carried to 94% completion (2 hr.), the yield of this isomerized alcohol was 31%. The remainder of the products that were identified were 4-methyl-4-pentenol (5% yield) and 4-methyl-1,4-pentanediol (22% yield). No 1-methylcyclopentene or methylenecyclopentane could be detected.

The 6-Methyl-6-heptenyl System.—In view of the foregoing, it was not surprising to find that formolysis of 6-methyl-6-heptenyl *p*-nitrobenzenesulfonate, m.p. 59.5–61°, instead of showing a predilection for seven-membered ring formation,[5] afforded the same products that were obtained on formolysis of the rearranged ester 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate (I), which is described in detail below. Only a trace of 1-methylcycloheptanol was detected.

The 6-Methyl-5-heptenyl System.—Corey and Sauers[6] have examined the formolysis of 6-methyl-5-heptenyl tosylate and found that the rate at 85° was 44 times that of the formolysis of *n*-hexyl tosylate, and that the product consisted mainly of cyclized material: 26% of a mixture of 1,2-dimethylcyclohexene, 1-isopropylcyclopentene (IV), and isopropylidenecyclopentane (V); and 42% of dimethylcyclopentylcarbinol (III).

We have examined the formolysis of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate (I), m.p. 59.5–61°, at 75°. The rate was about 20 times that of the formolysis of hexyl *p*-nitrobenzenesulfonate. The participation of the double bond in the solvolysis of the former substance was also reflected in the high yield of cyclic products. After 6 min. at 75°, the reaction was 80% complete, and the product consisted of 7% 1-isopropylcyclopentanol (II), 30% of dimethylcyclopentylcarbinol (III), 23% of 1-isopropylcyclopentene (IV), 30% of isopropylidenecyclopentane (V), 5% of 2,2-dimethylcyclohexanol (VI), and 4% of 6-methyl-5-heptenol. The identity of the alcohol components was determined by peak enhancement experiments on two different columns with authentic samples prepared by previously described procedures. The identity of the major alcohol fractions, dimethylcyclopentylcarbinol and 2,2-dimethylcyclohexanol, was also confirmed by isolation using preparative vapor phase chromatography and subsequent comparison of the infrared spectra with those of authentic samples. The identity of the previously described hydrocarbon components, 1-isopropylcyclopentene (IV) and isopropylidenecyclopentane (V), was determined by peak enhancement experiments on two different columns with authentic samples. The isopropylidenecyclopentane was also isolated by preparative vapor phase chromatography, and confirmation of its identity was obtained by infrared spectral comparison with authentic material and by preparation of the dibromo derivative, which melted at 67–69°, alone and on admixture with an authentic sample.



In addition to the solvolysis products enumerated above, trace amounts of *cis*- and *trans*-1,2-dimethylcyclohexanol and 2,3-dimethylcyclohexene were detected by vapor phase chromatographic peak enhancement experiments. 1,2-Dimethylcyclohexene had the same retention time as isopropylidenecyclopentane on the columns examined so that it was not possible to ascertain the presence or absence of the former substance, although it is a reasonable product of the solvolysis reaction.

Further experiments showed that in all probability the primary cyclization products were exclusively those resulting from five-membered ring formation, and that the 2,2-dimethylcyclohexanol (VI) was an artifact arising from rearrangement of the five-membered ring substances. Thus as the reaction time was increased (see Table I in Experimental section), the yield of the dimethylcyclohexanol (VI) was increased at the expense of the five-ring compounds. Indeed, after 10 hr. at 75°, the yield of VI was 91%. Precedent for this type of rearrangement is found in the terpene literature.[7]

(3) We have learned in a private communication from Professor P. D. Bartlett that this expectation indeed has been realized in his laboratory when acetic was used instead of formic acid for the solvolysis.

(4) *Cf.* the solvolysis of 4-methyl-3-pentenyl tosylate: J. B. Rogan, *J. Org. Chem.*, **27**, 3910 (1962).

(5) *Cf.* the formolysis of 6-heptenyl *p*-nitrobenzenesulfonate (ref. 2) which gives about 1% of cycloheptanol in addition to 66% heptenol.

(6) C. K. Sauers, Ph.D. Thesis, University of Illinois, 1957.

(7) P. de Mayo, "The Higher Terpenoids," Interscience Publishers, Inc., New York, N. Y., 1959, Chapters 3 and 4. See, for example, the acid-catalyzed rearrangement of lupenone into δ-amyrenone: T. R. Ames, T. G. Halsall, and E. R. H. Jones, *J. Chem. Soc.*, 450 (1951).

When a sample of 2,2-dimethylcyclohexanol, which was purified by preparative vapor phase chromatography, was submitted to the formolysis reaction conditions for 20 hr., small amounts of 1-isopropylcyclopentene, isopropylidenecyclopentane, and dimethylcyclopentylcarbinol were detected. The formation of these five-membered ring substances indicates that the aforementioned ring enlargement to 2,2-dimethylcyclohexanol is a reversible process.

Experimental[8]

Preparation of Materials. 5-Methyl-5-hexenol was prepared as previously described[9] by the lithium aluminum hydride reduction of 5-hexenoic acid. The product boiled at 87–89° (20 mm.), n^{23}D 1.440 (reported[9] b.p. 69–72° (11 mm.), n^{20}D 1.4415), and appeared to be 99% pure by vapor phase chromatography on a Craig succinate column at 126°.

5-Methyl-5-hexenyl *p*-Nitrobenzenesulfonate.—A mixture of 2.04 g. of the aforementioned 5-methyl-5-hexenol, 4.43 g. of *p*-nitrobenzenesulfonyl chloride, and 20 ml. of anhydrous pyridine was stirred at −20° for 4 hr. The mixture was then poured into 50 ml. of cold 10% hydrochloric acid and extracted with chloroform. The combined organic layers were washed with water, followed by saturated brine, and dried over anhydrous magnesium sulfate. The residue obtained upon evaporation of the solvents at reduced pressure was crystallized from ether–pentane to give 2.52 g. of the ester, m.p. 38.5–40.5°. Recrystallization from the same solvent pair gave pale yellow plates, m.p. 43–45°, $\lambda_{max}^{95\%\ EtOH}$ 250 mμ (ε 11,600).

Anal. Calcd. for $C_{13}H_{17}O_5NS$: C, 52.16; H, 5.73. Found: C, 52.4; H, 5.9.

5-Methyl-4-hexenol was prepared by the action of paraformaldehyde and the Grignard reagent from 4-methyl-3-pentenyl bromide.[10] After distillation through a short Vigreux column, the product was obtained as a colorless liquid, b.p. 94–95° (25 mm.), n^{21}D 1.450 (reported[11] b.p. 79° (15 mm.), n^{18}D 1.4482). Vapor phase chromatography on a Craig succinate column at 132° gave response for about 5% of an unidentified impurity.

5-Methyl-1,5-hexanediol.—A solution of 0.96 g. of the aforementioned 5-methyl-5-hexenol in 20 ml. of anhydrous formic acid was heated at 75° for 30 min. The mixture was then cooled, neutralized with 30% sodium hydroxide, saturated with potassium carbonate, and extracted with ether. The combined organic layers were washed with water, followed by saturated brine, and dried over anhydrous magnesium sulfate. The solution was concentrated to a volume of about 10 ml. and added to a suspension of 1.0 g. of lithium aluminum hydride in 50 ml. of ether. The mixture was allowed to stir overnight; then it was decomposed with dilute sulfuric acid and the aqueous layer was extracted with ether. The combined organic layers were washed with saturated brine and dried over anhydrous magnesium sulfate. The residue obtained upon removal of the solvent at reduced pressure was chromatographed on 40 g. of Florisil. The fraction eluted with 70% ether in petroleum ether was evaporatively distilled at 110° (40 μ) to give 0.4 g. of the diol as a viscous liquid, n^{20}D 1.457 (reported[11] n^{22}D 1.4556). The n.m.r. spectrum exhibited absorption for 6 protons as a singlet at δ = 1.20 p.p.m. (*gem*-dimethyl protons), 6 protons as a multiplet centered at δ = 1.47 p.p.m. (methylene protons), and 2 protons as a multiplet centered at δ = 3.62 p.p.m. (CH_2O).

The bis-*p*-nitrobenzoate was obtained by treatment of the diol with *p*-nitrobenzoyl chloride in pyridine. Repeated recrystallizations from absolute ethanol gave pale brown needles, m.p. 130–131°.

Anal. Calcd. for $C_{21}H_{22}O_8N_2$: C, 58.61; H, 5.16; N, 6.51. Found: C, 58.8; H, 5.1; N, 6.75.

4-Methyl-4-pentenol was prepared by the action of ethylene oxide on methallylmagnesium chloride.[12] Distillation through a 2-ft. Podbielniak-type column gave a colorless product, b.p. 89–90° (47 mm.), n^{20}D 1.437 (reported[13] b.p. 67.5–68° (19 mm.), n^{20}D 1.4372). Vapor phase chromatography on a Craig succinate column at 91° indicated response for a single component.

4-Methyl-4-pentenyl *p*-nitrobenzenesulfonate was prepared as described above for the 5-methyl-5-hexenyl ester. Crystallization of the crude product from ether–pentane gave, in 50% yield, pale yellow plates, m.p. 44–45°, $\lambda_{max}^{95\%\ EtOH}$ 250 mμ (ε 11,700). Repeated recrystallizations raised the m.p. to 44.5–45.5°.

Anal. Calcd. for $C_{12}H_{15}O_5NS$: C, 50.52; H, 5.30; N, 4.91. Found: C, 50.2; H, 5.4; N, 5.2.

1-Methylcyclopentanol was prepared by the reaction of methylmagnesium iodide on cyclopentanone. Distillation of the product through a 2-ft. Podbielniak-type column gave a colorless liquid, b.p. 66–67° (35 mm.), m.p. 35–36° (reported[14] b.p. 81° (100 mm.), m.p. 36°). Vapor phase chromatography on a Craig succinate column at 92° indicated a single component.

4-Methyl-3-pentenol[4] was obtained as a colorless liquid, b.p. 106–107° (110 mm.), n^{22}D 1.445 (reported[4] b.p. 105–105.5° (110 mm.), n^{25}D 1.4443). Vapor phase chromatography on a Craig succinate column at 91° gave response for a single component.

4-Methyl-1,4-pentanediol.—A 1.0-g. sample of the aforementioned 4-methyl-4-pentenol was treated with 25 ml. of anhydrous formic acid as described above for the preparation of 5-methyl-1,5-hexanediol. The product, on distillation through a Kontes micro-head, amounted to 0.43 g. of colorless diol, b.p. 78–80° (0.4 mm.), n^{20}D 1.450 (reported[15] b.p. 126–127° (16 mm.), n^{20}D 1.4492). The bis-*p*-nitrobenzoate was obtained from ethanol as pale brown needles, m.p. 157–158.5° (reported[16] 158°).

Methylenecyclopentane was prepared by an adaptation of the procedure for the production of methylenecyclohexane.[17] The product, after distillation through a 2-ft. Podbielniak-type column, was shown by vapor phase chromatography on an SE-30 column to be contaminated with unidentified impurities. A pure specimen, n^{20}D 1.434 (reported[18] 1.4344), was obtained by preparative vapor phase chromatography on a 30% SE-30 column at 68°.

6-Methyl-6-heptenol. a. *Via* **5-Methyl-5-hexenyl Bromide.**—A solution of 11.4 g. of the aforementioned 5-methyl-5-hexenol in 7.9 g. of pyridine and 10 ml. of pentane was added slowly with stirring to a solution of 10.8 g. of phosphorus tribromide in 20 ml. of pentane. The reaction mixture was cooled (−20 to −10°) during the addition, and then was allowed to warm to room temperature. After standing overnight, the mixture was poured into ice–water, and the aqueous phase was extracted with ether. The combined organic layers were washed with water, saturated sodium bicarbonate solution, then with saturated brine, and dried over anhydrous potassium carbonate. The residue obtained on evaporation of the solvent was distilled through a Claisen head to give 2.23 g. of the bromide as a colorless liquid, b.p. 76° (23 mm.), n^{23}D 1.4675.

Anal. Calcd. for $C_7H_{13}Br$: Br, 45.12. Found: Br, 45.1.

A solution of 1.7 g. of the aforementioned bromide in 50 ml. of anhydrous ether was added to a mixture of 0.26 g. of magnesium turnings, a small crystal of iodine, and 10 ml. of ether. The mixture was heated at reflux for 1 hr., and then 0.35 g. of paraformaldehyde was added. This mixture was stirred overnight at room temperature; then 20 ml. of saturated ammonium chloride solution was added. The aqueous phase was extracted with ether, and the combined organic layers were washed with water, followed by saturated brine, and dried over magnesium sulfate. The residue obtained on removal of the solvent by distillation through an 8-in. Vigreux column was distilled through a short Claisen head to give 0.7 g. of a liquid mixture, b.p. 85–104° (22 mm.).

(8) Melting points were determined on a Kofler hotstage microscope. Nuclear magnetic resonance spectra were determined under the supervision of Dr. L. J. Durham on a Varian Associates A-60 n.m.r. spectrometer. Unless indicated otherwise, deuteriochloroform was employed as the solvent with tetramethylsilane as the internal reference. The chemical shifts are reported as δ-values in p.p.m. relative to tetramethylsilane = 0. Vapor phase chromatographic analyses were conducted on an Aerograph (A-600) gas chromatograph equipped with a hydrogen flame ionizer detector and a disk chart integrator. Nitrogen and hydrogen flow rates were approximately 25 ml./min. An Aerograph Autoprep (A-700) chromatograph was used for the preparative vapor phase chromatography experiments.

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Preparative vapor phase chromatography on a Carbowax 20M column at 145° gave 0.26 g. of pure 6-methyl-6-heptenol, $n^{23}D$ 1.450 (reported[11] 1.4489).

b. From 1-Tetrahydropyranyloxy-6-methyl-6-heptene.—This ether was prepared by the reaction of 4-tetrahydropyranyloxybutylmagnesium chloride and methallyl chloride, followed by acid-catalyzed cleavage as described by Crisan,[11] except that oxalic was used in place of phosphoric acid for the latter step. The product on distillation through a 12-in. micro-Podbielniak-type column was obtained as a colorless liquid, b.p. 89–92° (13 mm.), $n^{20}D$ 1.451 (reported[11] b.p. 89–90° (14 mm.), $n^{23}D$ 1.4489). Vapor phase chromatography on a Craig succinate column at 125° indicated that this product was approximately 98% pure.

6-Methyl-6-heptenyl *p*-nitrobenzenesulfonate was prepared as described above for the 5-methyl-5-hexenyl ester. Crystallization of the crude product from ether–pentane gave, in 72% yield, pale yellow plates, m.p. 57–59°. Recrystallization gave material, m.p. 59.5–61°, $\lambda_{max}^{95\%\ EtOH}$ 250 mμ (ε 11,500).

Anal. Calcd. for $C_{14}H_{19}O_5NS$: C, 53.65; H, 6.11; N, 4.47. Found: C, 53.7; H, 6.1; N, 4.7.

1-Methylcycloheptanol was prepared by the action of methylmagnesium iodide on cycloheptanone. Distillation through a 12-in. micro-Podbielniak-type column afforded a colorless liquid, b.p. 85–87° (20 mm.), $n^{20}D$ 1.4595 (reported[19] b.p. 82–83.5° (20 mm.), $n^{20}D$ 1.4690). Vapor phase chromatography on a Craig succinate column at 125° indicated a single component.

6-Methyl-5-heptenol was prepared by the action of ethylene oxide on the Grignard reagent from 4-methyl-3-pentenyl bromide.[10] The product on distillation through a 2-ft. Podbielniak-type column was obtained as a colorless liquid, b.p. 80–94° (16 mm.). Vapor phase chromatography on a Craig succinate column indicated the presence of 10% of an unidentified impurity. Pure 6-methyl-5-heptenol was obtained by preparative vapor phase chromatography on a Carbowax 20M column at 150°, $n^{22}D$ 1.450 (reported[20] $n^{20}D$ 1.4510), b.p. 94–95° (16 mm.).

6-Methyl-5-heptenyl *p*-nitrobenzenesulfonate was prepared as described above for the 5-methyl-5-hexenyl ester. Crystallization of the crude product from ether–pentane gave, in 54% yield, pale yellow plates, m.p. 59.5–61°, $\lambda_{max}^{95\%\ EtOH}$ 250 mμ (ε 11,500). The melting point was not raised by further recrystallizations.

Anal. Calcd. for $C_{14}H_{19}O_5NS$: C, 53.65; H, 6.11; N, 4.47. Found: C, 53.9; H, 6.1; N, 4.6.

Isopropylcyclopentanol was prepared by the action of isopropylmagnesium bromide on cyclopentanone, and the product was purified by distillation through a 2-ft. Podbielniak-type column, followed by preparative vapor phase chromatography on a Carbowax 20M column at 120°, to give a colorless solid, m.p. 21–22°, $n^{20}D$ 1.458 (reported[21] m.p. 22°, $n^{25}D$ 1.4560).

Dimethylcyclopentylcarbinol was prepared by the reaction of methylmagnesium iodide on methyl cyclopentanecarboxylate.[22] The product was purified by distillation through a 12-in. micro-Podbielniak-type column to give a colorless liquid, b.p. 83–84° (35 mm.), $n^{22}D$ 1.458 (reported[23] b.p. 100° (73 mm.), $n^{20}D$ 1.4591). Vapor phase chromatography over a Craig succinate column at 125° indicated a single component.

1-Isopropylcyclopentene and Isopropylidenecyclopentane.—A mixture of 1.5 g. of the aforementioned dimethylcyclopentylcarbinol and 1 drop of concentrated sulfuric acid was heated at 165° in a flask connected to a 6-in. Vigreux distillation head. The distillate was diluted with pentane, washed with water, followed by saturated brine, and dried over anhydrous magnesium sulfate–neutral alumina. The solvent was removed by distillation through a 2-ft. Podbielniak-type column, and the residue was distilled through a short Claisen head to give 0.8 g. of a mixture of 40% of 1-isopropylcyclopentene, 13% of isopropenylcyclopentane, and 47% of isopropylidenecyclopentane as determined by vapor phase chromatographic analysis on an SE-30 column at 70°. The mixture of olefins was separated by preparative vapor phase chromatography on a 30% SE-30 column at 112°. The fraction with retention time 26.5 min. was 1-isopropylcyclopentene, $n^{20}D$ 1.444 (reported[23] 1.4443). The n.m.r. spectrum in carbon tetrachloride solution exhibited absorption for 6 protons as a doublet centered at δ = 1.05 p.p.m. (*gem*-dimethyl protons) and 1 proton as a singlet at δ = 5.25 p.p.m. (vinyl proton). The fraction with retention time 30.5 min. was isopropenylcyclopentane, $n^{20}D$ 1.451 (reported[24] 1.4545), λ_{max}^{film} 6.08 μ (C=C) and 11.26 (C=CH_2). The fraction with retention time 40.0 min. was isopropylidenecyclopentane, $n^{20}D$ 1.459 (reported[23] 1.4593). The infrared spectrum was identical with that reported[25] for isopropylidenecyclopentane, and the n.m.r. spectrum showed no absorption for vinyl protons. The dibromide of this last hydrocarbon was obtained from absolute ethanol as colorless plates, m.p. 68.5–69.5° (reported[25] 68°).

2,2-Dimethylcyclohexanol was prepared by lithium aluminum hydride reduction of the corresponding ketone. The product was purified by preparative vapor phase chromatography on a Carbowax 20M column at 136° to give a colorless liquid, $n^{20}D$ 1.465 (reported[26] 1.4646).

A mixture of *cis*- and *trans*-**1,2-dimethylcyclohexanol** was prepared by the reaction of methylmagnesium bromide with 2-methylcyclohexanone.[27] Vapor phase chromatographic analysis of the product on a Craig succinate column at 125° indicated a major fraction (the *trans* isomer) with retention time 5.7 min., and a minor fraction (the *cis* isomer) with retention time 7.4 min.

1,2-Dimethylcyclohexene.—A mixture of this olefin and 2,3-dimethylcyclohexene was prepared as previously described[28] by dehydration of the aforementioned 1,2-dimethylcyclohexanol. Preparative vapor phase chromatography of the distilled product on a Carbowax 20M column at 72° gave pure 1,2-dimethylcyclohexene, $n^{25}D$ 1.459 (reported[28] 1.4587).

Solvolysis Experiments. 5-Methyl-5-hexenyl *p*-Nitrobenzenesulfonate.—To 40 ml. of anhydrous formic acid preheated to 75° were added 0.109 g. of anhydrous sodium formate and 0.239 g. of 5-methyl-5-hexenyl *p*-nitrobenzenesulfonate, m.p. 43–45°. The solution was heated under an atmosphere of nitrogen in a bath maintained at 75 ± 2° for 2 hr. The reaction mixture was then rapidly cooled and divided into two equal parts. One of the portions was diluted with 10 ml. of ether and neutralized with 60 ml. of 30% sodium hydroxide, then saturated with potassium carbonate, and finally extracted thoroughly with ether. The combined ethereal extracts were washed with saturated brine, dried over anhydrous magnesium sulfate, and concentrated through a 2-ft. Podbielniak-type column to a volume of exactly 10 ml. A 1-ml. aliquot was used to determine the extent of reaction (65%) by ultraviolet spectroscopy, as already described for the 5-hexenyl ester.[2] The remaining 9 ml. of the ether solution was added dropwise to about 0.5 g. of lithium aluminum hydride in 25 ml. of anhydrous ether. The mixture was heated under reflux for 1 hr., then cooled in an ice–salt bath while 10 ml. of 2 *N* sulfuric acid was added. The aqueous layer was separated and extracted with ether, and the combined organic phases were washed with saturated brine, dried over magnesium sulfate, and concentrated as described above to exactly 5 ml. for analysis of the alcoholic products.

The other portion of the formic acid solution was diluted with 10 ml. of carbon disulfide and neutralized with 60 ml. of 30% sodium hydroxide. The solution was then saturated with potassium carbonate and extracted with an additional 35 ml. of carbon disulfide in 5 portions. The carbon disulfide extracts were washed with saturated brine, dried over anhydrous sodium sulfate, and diluted to exactly 50 ml. for the analysis of hydrocarbons, as described below.

The formolysis products in the 5-ml. ether solution were analyzed for alcohols by vapor phase chromatography on a Craig succinate column operated at 112° or at 175°. The products were identified by peak enhancement with authentic samples of 1-methylcyclohexanol (retention time 6.5 min. at 112°), 5-methyl-4-hexenol (13.7 min. at 112°), and 5-methyl-1,5-hexanediol (13 min. at 175°). The absolute yields of 1-methylcyclohexanol and 5-methyl-4-hexenol were determined by adding 1 ml. of a standard (3.84×10^{-2} *M*) solution of cyclohexanol to a 2-ml. aliquot of the 5-ml. ether solution. The relative peak areas were: 1-methylcyclohexanol, 1.00 (retention time 6.5 min. at 112°);

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cyclohexanol, 1.23 (8.5 min.); and 5-methyl-5-hexenol, 0.35 (13.7 min.). These values were then corrected for the relative detector responses (1.0:0.88:0.66, respectively) which were obtained from mixtures containing known concentrations of the three components. The concentration of 1-methylcyclohexanol was calculated to be 1.37×10^{-2} *M*, corresponding to an absolute yield (corrected for unreacted *p*-nitrobenzenesulfonate) of 29%, and that of 5-methyl-5-hexenol was calculated to be 0.73×10^{-2} *M*, or a 16% yield. The absolute yield of 5-methyl-1,5-hexanediol was determined by adding 0.6 ml. of a standard (2.4×10^{-2} *M*) solution of 4-methoxycyclohexanol to a 2-ml. aliquot of the 5-ml. ether solution. The relative peak areas were: 4-methoxycyclohexanol, 4.71 (retention time 8.2 min. at 175°), and 5-methyl-1,5-hexanediol, 1.00 (13.0 min.). These values were then corrected for relative detector response (2.97:1.00, respectively). Thus, the concentration of the 5-methyl-1,5-hexanediol was calculated to be 0.45×10^{-2} *M*, corresponding to an absolute yield (corrected for unreacted *p*-nitrobenzenesulfonate) of 10%.

The 50-ml. carbon disulfide solution was analyzed for hydrocarbons by vapor phase chromatography on an SE-30 column operated at 50°. A single peak was obtained and, as shown by peak enhancement experiments, this corresponded to 1-methylcyclohexene (retention time 15.0 min.). The absolute yield of 1-methylcyclohexene was determined by vapor phase chromatographic analysis of a 25-ml. aliquot containing exactly 9.5 mg. of added 1-methylcyclohexene. The relative area of the 1-methylcyclohexene peak increased from 0.47 to 4.0 (relative to an unidentified solvent peak used for internal standardization). The amount of 1-methylcyclohexene present in the carbon disulfide solution, therefore, was 2.6 mg., corresponding to a 10% yield.

In another solvolysis experiment conducted exactly as described above except that ether was used for extraction of the total reaction mixture, the product was submitted to preparative vapor phase chromatography on a Carbowax 20M column at 150°, and the 5-methyl-4-hexenol and the 1-methylcyclohexanol fractions were separated. The infrared spectrum of the 5-methyl-4-hexenol was identical with that of the authentic specimen except for trace absorption at 6.1 and 11.3 μ (=CH_2), indicating the presence of traces of 5-methyl-5-hexenol. The two isomeric unsaturated alcohols were not separable on the vapor phase chromatographic columns used The infrared spectrum of 1-methylcyclohexanol was identical with that of a corresponding authentic sample, thus confirming the identity of the cyclized product.

In another run performed as described above except that the molarity of sodium formate was increased from 0.04 to 1.0, the following yields of products were determined: 20% 1-methylcyclohexanol, 17% 5-methyl-4-hexenol, 16% 5-methyl-1,5-hexanediol, and 20% 1-methylcyclohexene.

4-Methyl-4-pentenyl *p*-Nitrobenzenesulfonate.—To 40 ml. of anhydrous formic acid preheated to 75° were added 0.109 g. of anhydrous sodium formate and 0.228 g. of 4-methyl-4-pentenyl *p*-nitrobenzenesulfonate, m.p. 43.5–44.5°. The solution was heated under an atmosphere of nitrogen in a bath maintained at 75 ± 2° for 2 hr. The mixture was rapidly cooled and divided into two equal parts which were treated exactly as described above for the 5-methyl-5-hexenyl ester. The extent of solvolysis was determined to be 96% by ultraviolet spectroscopy.

The 5-ml. ether solution of the formolysis products (after lithium aluminum hydride treatment) was used for the analysis of alcohols, as described for the 5-methyl-5-hexenyl ester, except that a Carbowax 20M column was used at 93 and 175°. By peak enhancement experiments with authentic 1-methylcyclopentanol (retention time 7.4 min. at 93°), 4-methyl-3-pentenol (19 min. at 93°), 4-methyl-4-pentenol (20.5 min. at 93°), and 4-methyl-1,4-pentanediol (12 min. at 175°), it was apparent that the product consisted principally of the second and fourth of these substances. The yield of monohydric alcohols was determined by adding a known amount of 1-methylcyclopentanol, and the yield of the diol was determined by adding a known amount of 4-methoxycyclohexanol as described for the 5-methyl-5-hexenyl ester. The relative detector responses for 4-methyl-3-pentenol and 1-methylcyclopentanol were 1.0:1.64, respectively, and for 4-methoxycyclohexanol and 4-methyl-1,4-pentanediol it was 2.3:1.0, respectively. Thus the yield of 4-methyl-3-pentenol was shown to be 31% and that of 4-methyl-1,4-pentanediol to be 22%. The yield of 4-methyl-4-pentenol was 5%; 1-methylcyclopentanol was detected in trace amounts. No dimethylcyclopropylcarbinol (6 min. at 93°) was detected.

The 50-ml. carbon disulfide solution was analyzed for hydrocarbons on an Apiezon L column at 30°. The chromatogram showed no significant quantity of any hydrocarbon. The poor material balance was probably the result of incomplete isolation of the water-soluble diol.

Another experiment was carried out on a 1.14-g. scale. The procedure was identical with that described above except that ether was used for extraction of the total reaction mixture, and the product was submitted to preparative vapor phase chromatography on a Carbowax 20M column at 140°. A sample of 4-methyl-3-pentenol which was contaminated with about 5% of 4-methyl-4-pentenol was collected. The infrared spectrum of the sample was identical with that of the authentic 4-methyl-3-pentenol except for traces of terminal methylene absorption at 6.1 and 11.3 μ.

The solvolysis mixture from the large-scale experiment was also submitted to quantitative analysis, and the following yields were calculated: 30% of 4-methyl-3-pentenol, 4% of 4-methyl-4-pentenol, and 19% of 4-methyl-1,4-pentanediol.

6-Methyl-5-heptenyl *p*-Nitrobenzenesulfonate.—The following constitutes a detailed description of run a of the formolysis of this ester as summarized in Table I. Runs b and e were conducted in an identical fashion except for the differences in reaction time summarized in the table. Runs c and d were also conducted as described for runs a, b, and e except that the work-up procedure involved dividing the formolysis solution into two portions and extracting separately with ether and carbon disulfide as described above for the formolysis of the 5-methyl-5-hexenyl ester.

To 40 ml. of anhydrous formic acid preheated to 75° were added 0.109 g. of anhydrous sodium formate and 0.250 g. of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate, m.p. 59.5–61°. The solution was heated under an atmosphere of nitrogen in a bath maintained at 75 ± 2° for 6 min. The mixture was then rapidly cooled, diluted with 20 ml. of pentane, and neutralized with 120 ml. of 30% sodium hydroxide. The mixture was saturated with potassium carbonate, and the aqueous phase was extracted thoroughly with pentane. The combined organic layers were washed with saturated brine, dried over magnesium sulfate, and concentrated to exactly 10 ml. through a 2-ft. Podbielniak-type column. A 1-ml. aliquot was used for determining the extent of reaction (80%) by ultraviolet spectroscopy. A 5-ml. aliquot was added dropwise to approximately 0.5 g. of lithium aluminum hydride in 25 ml. of anhydrous ether. The mixture was heated at reflux for 1 hr., and then cooled in an ice bath while 10 ml. of 2 *N* sulfuric acid was added. The aqueous layer was separated and extracted with ether, and the combined organic layers were washed with saturated brine, dried over magnesium sulfate, and concentrated to exactly 5 ml. for analysis of the alcoholic products. The remaining 4 ml. of pentane solution was used for analysis of hydrocarbons as described below.

The formolysis mixture in the 5-ml. ether solution (after lithium aluminum hydride treatment) was analyzed for alcohols by vapor phase chromatography on a Craig succinate column at 125°. The products were identified by peak enhancements with authentic samples of 1-isopropylcyclopentanol (retention time 6.0 min.), dimethylcyclopentylcarbinol (6.4 min.), 2,2-dimethylcyclohexanol (8.2 min.), and 6-methyl-5-heptenol (13.2 min.). Under these conditions the retention time of *trans*-1,2-dimethylcyclohexanol was 5.6 min. and of *cis*-1,2-dimethylcyclohexanol was 7.3 min. Peak enhancement experiments were also performed on a Carbowax 20M column at 112° for 1-isopropylcyclopentanol (8 min.), dimethylcyclopentylcarbinol (9 min.), and 2,2-dimethylcyclohexanol (13 min.). The absolute yields of the alcoholic components were determined by vapor phase chromatographic analysis on a Craig succinate column at 125° by using a standard solution of 6-methyl-5-heptenol as described above for the formolysis of the 5-methyl-5-hexenyl ester. The relative detector response for 1-isopropylcyclopentanol, dimethylcyclopentylcarbinol, 2,2-dimethylcyclohexanol, and 6-methyl-5-heptenol were 1.5:1.5:1.1:1.0, respectively. The absolute yields were determined as described above and are summarized in Table I.

The remaining 4 ml. of pentane solution was analyzed for hydrocarbon products. Peak enhancement experiments on an SE-30 column at 70° with authentic samples indicated the presence of 1-isopropylcyclopentene (retention time 10 min.) and isopropylidenecyclopentane (16 min.). Under these conditions the retention time of 2,3-dimethylcyclohexene was 12.5 min. and of 1,2-dimethylcyclohexene was 15.7 min. Peak enhancement experiments were also performed on an Apiezon L column at 80°: 1-isopropylcyclopentene (retention time 10.8 min.) and isopropylidenecyclopentane (18 min.). The product composition of the

TABLE I

Run	Time, hr.	Extent of reaction, %	Yield, % II	III	VI	1,2-Dimethylcyclohexanol	6-Methyl-5-heptenol	IV	V
Formolysis of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate[a]									
a	0.1	80	7	30	5	...	4	23	30
b	0.25	96	5	13	10	...	..	21	28
c	1	99	5	9	37	...	..	19	24
d	5	100	1	2	78	Trace	..	5	7
e	10	100	0	Trace	91	Trace	..	1	2
Formolysis of 6-methyl-6-heptenyl *p*-nitrobenzenesulfonate									
f	1	96	4	10	37	(1-Methylcycloheptanol: trace)		19	24
g	6	98	0	Trace	95	(1-Methylcycloheptanol: trace)		..	..

[a] 0.02 *M* substrate and 0.04 *M* HCOONa in anhydrous HCOOH at 75°.

two hydrocarbons was approximately 45 and 55%, respectively. The absolute yields were determined on an SE-30 column at 70° by comparison of the peak areas produced from injections of the pentane solution and a standard (1.5×10^{-2} *M*) solution of *ca.* 45% 1-isopropylcyclopentene and *ca.* 55% isopropylidenecyclopentane. Thus 2-λ injections of the standard solution gave response for 165 units of area as compared with 186 units of area for the pentane solution. Therefore the combined concentration of the two hydrocarbons was 1.7×10^{-2} *M*, corresponding to an absolute yield of 53%, or 23% 1-isopropylcyclopentene and 30% isopropylidenecyclopentane.

Another formolysis experiment was carried out on a 0.626-g. scale. The procedure was identical with that described above except that ether was used for extraction of the entire formolysis reaction mixture, and the product was submitted to preparative vapor phase chromatography on a Carbowax 20M column at 130°. The alcoholic components, dimethylcyclopentylcarbinol and 2,2-dimethylcyclohexanol, were collected and their infrared spectra shown to be identical with those of the corresponding authentic materials. The isopropylidenecyclopentane fraction was also collected, and its identity was confirmed by infrared spectral comparison with an authentic sample and by preparation of its dibromo derivative, which was obtained from ethanol as colorless plates, m.p. 67–69°, undepressed on admixture with the authentic material described above.

2,2-Dimethylcyclohexanol.—A solution of 28 mg. of 2,2-dimethylcyclohexanol (purified as described above by preparative vapor phase chromatography), 44 mg. of *p*-nitrobenzenesulfonic acid (Eastman Kodak, practical grade), and 30 mg. of anhydrous sodium formate in 11 ml. of anhydrous formic acid was heated under an atmosphere of nitrogen at 75° for 20 hr. The reaction mixture was processed and the product was analyzed just as described above for run a of the formolysis of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate. The absolute yields of the alcoholic products were determined to be 76% of 2,2-dimethylcyclohexanol (retention time 11.4 min. on Craig succinate at 114°), *ca.* 1% of *trans*-1,2-dimethylcyclohexanol (7.8 min.), *ca.* 1% of *cis*-1,2-dimethylcyclohexanol (10.0 min.), and a trace of dimethylcyclopentylcarbinol (8.1 min.). The olefinic products consisted of *ca.* 1% of 1-isopropylcyclopentene (retention time 10 min. on SE-30 at 70°), *ca.* 0.5% of 2,3-dimethylcyclohexene (12.0 min.), and 2% of either pure isopropylidenecyclopentane (16.0 min.) or a mixture of isopropylidenecyclopentane and 1,2-dimethylcyclohexene (15.7 min.).

6-Methyl-6-heptenyl *p*-Nitrobenzenesulfonate.—An experiment with this substrate was conducted exactly as described above for runs c and d of the formolysis of the 6-methyl-5-heptenyl ester. The results of the analysis are summarized under run f, Table I.

Another experiment was performed exactly as described above for run a of the formolysis of the 6-methyl-5-heptenyl ester except that the reaction mixture was not divided and no analysis was made for hydrocarbons. The results are summarized under run g, Table I.

Another experiment was conducted in a fashion identical with that of run g except on a larger scale (0.626 g. of the ester, m.p. 59.5–61°, 0.272 g. of sodium formate, and 100 ml. of formic acid). 2,2-Dimethylcyclohexanol was isolated by evaporative distillation in 60% yield. The infrared spectrum was identical with that of authentic material. The n.m.r. spectrum of the 2,2-dimethylcyclohexanol isolated from the formolysis exhibited absorption for 6 protons as a doublet centered at $\delta = 0.9$ p.p.m. (*gem*-dimethyl protons), 1 proton as a singlet at $\delta = 8.12$ p.p.m. (–OH proton), and 1 proton as a multiplet centered at $\delta = 3.25$ p.p.m. (proton α to –OH).

Relative Rates.—These experiments were carried out exactly as already described in detail.[2] The times required for disappearance of one-half of the alkenyl *p*-nitrobenzenesulfonates (0.02 *M* solution in anhydrous formic acid containing 0.04 *M* sodium formate) at 75° were: 5-methyl-5-hexenyl, 70 min.; 4-methyl-4-pentenyl, 30 min.; and 6-methyl-6-heptenyl, 4 min.

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[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210]

A New Cyclization Reaction Leading to Epoxides of Aromatic Hydrocarbons[1,2]

BY MELVIN S. NEWMAN AND SHOSHANA BLUM

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Treatment *o,o'*-diformylbiphenyl with trisdimethylaminophosphine yields 9,10-dihydro-9,10-epoxyphenanthrene (I) in high yield. Two other dialdehydes are cyclized to the epoxides II and III. These three epoxides represent the first epoxides of aromatic hydrocarbons that have been synthesized. On treatment with acid, the epoxides isomerize to phenolic compounds.

Although epoxy derivatives of aromatic hydrocarbons[2] have been postulated as intermediates in the metabolism of polycyclic aromatic hydrocarbons,[3] such compounds have as yet not been prepared.[4]

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(2) The term epoxides of aromatic hydrocarbons means that if the oxygen atom is removed, an aromatic ring is produced from that ring which contains the two carbons to which the oxygen was attached.

(3) See E. Boyland and P. Sims, *Biochem. J.*, **84**, 571 (1962); **90**, 391 (1964), and earlier references therein.

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