equivalent calcd. for $C_{17}H_{22}O_2$ 256.1, found 258 and 260. The ester had an intense carbonyl band at 5.86 μ; the n.m.r. spectrum in carbon tetrachloride showed complex multiplets at 9.2–9.75 (12 protons), 8.35–8.85 (3 protons), 2.05–2.30 (2 protons), and 2.50–2.80 τ (3 protons).

Rearrangement of Tricyclopropylcarbinyl Benzoate (IV, X = B).—Five grams of the ester was heated at 100° for 30 min. During this time, the n.m.r. spectrum changed progressively to a spectrum with bands at: complex multiplet at 9.1–9.85 (8 protons), multiplet at 8.2–8.7 (2 protons), quartet centered at 7.47 (J = 7.0 c.p.s., 2 protons), triplet at 5.8 (J = 7.0 c.p.s., 2 protons), triplet at 4.95 (J = 7.0 c.p.s., 1 proton), and complex multiplets at 1.95–2.3 and 2.5–2.95 τ (2 and 3 protons, respectively). The product, **4,4-dicyclopropylbut-3-en-1-yl benzoate**, distilled from 115–120° at 0.04 mm.; the distillate was contaminated with benzoic anhydride, which was removed by chromatography on Florisil, with pentane as eluent. Purified product had bands at 5.86 (strong) and 6.08 μ (weak).

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.44; H, 7.68.

Dicyclopropylisopropylcarbinyl Benzoate (III, X = B).—This ester was prepared by a method analogous to that described above for IV (X = B). The yield was nearly quantitative, but the ester could not be distilled without decomposition and rearrangement. The infrared spectrum had a band at 5.86 μ and no bands in the 6.0–6.2 μ region. The n.m.r. spectrum in carbon tetrachloride consisted of a complex multiplet from 9.2–9.7 (8 protons), a sharp doublet centered at 8.92 (J = 7 c.p.s., 6 protons) overlapped by a complex multiplet from 8.6–9.1 (2 protons), a septet at 6.76 (J = 7 c.p.s., 1 proton), and complex multiplets from 2.0–2.25 and 2.5–2.8 τ (2 and 3 protons, respectively). The purity of samples used in kinetic experiments was about 90%, as determined by saponification equivalent (the impurity was usually ligroin, used as a solvent when the ester was stirred with activated alumina, to remove traces of benzoyl chloride which might be present).

The ester was heated for varying periods of time, neat, at 100°, and the n.m.r. spectrum examined periodically. After 70 min., bands appeared around 4.9 and 5.8 τ and increased slowly in intensity (about 30% rearrangement in 290 min.).

Kinetic Experiments. Materials.—Dioxane, methanol, and carbon dioxide-free water were purified and prepared by standard procedures. Sodium hydroxide solution (approximately 0.01 N) in 70% aqueous dioxane was used as the titrant. It was standardized against primary standard benzoic acid dissolved in aqueous dioxane having the same percentage composition as that used in the particular kinetic experiment. The indicator was phenolphthalein. If the kinetic run lasted over 3 hr., the base was restandardized. The titrant was protected by Ascarite from atmospheric carbon dioxide, and all titrations were performed in a nitrogen atmosphere. **Procedure.**—Approximately 0.001 mole of ester was accurately weighed into a dry 100-ml. volumetric flask. At zero time, 100 ml. of temperature-equilibrated solvent was pipetted into the flask, and the solution thoroughly mixed. At various times, 5-ml. aliquots were withdrawn (in temperature-equilibrated pipets), quenched by adding to 5 ml. of absolute acetone at −10°, and immediately titrated, at ice–salt bath temperature. Usually 10–15 points were taken for each run, and at least two runs were made under each set of conditions.

Solvolysis Products from Tricyclopropylcarbinyl Benzoate. Absolute Methanol.—Tricyclopropylcarbinyl benzoate (1.167 g., 4.57 mmoles) dissolved in 100 ml. of absolute methanol was kept at 25° for 48 hr. The residue, after removal of solvent *in vacuo* at room temperature, consisted of white needles (benzoic acid) and a colorless oil. The latter was taken up in pentane, washed twice with 10 ml. of 1 N sodium hydroxide and water, and dried over magnesium sulfate. After removal of solvent, the residue (nearly quantitative yield) had an infrared spectrum with an intense broad infrared band at 9.2 μ, with no bands in the 2.75–3.0 or 6–6.2 μ regions. Its n.m.r. spectrum consisted of a single sharp peak at 6.75 (3 protons) and a complex multiplet from 9.0–9.9 τ (15 protons). The infrared spectrum had a trace carbonyl peak at 5.8 μ, and barely detectable in the n.m.r. spectrum were weak bands (too small for accurate integration) in the aromatic and vinyl proton regions. The product is therefore **tricyclopropylcarbinyl methyl ether** contaminated with about 2% of unsaturated aromatic ester, presumably 4,4-dicyclopropylbut-3-en-1-yl benzoate. Similar results were obtained in 95% dioxane–5% methanol solvent. **95% Aqueous Dioxane.**—Tricyclopropylcarbinyl benzoate (10 g., 0.066 mole) in 300 ml. of 95% dioxane–5% water was kept at 25° for 19 hr. The solvent was removed *in vacuo* mainly at room temperature, with slight warming on a steam bath at the end. After taking up the residue in pentane, washing with alkali and water, and drying with magnesium sulfate, a residue was obtained whose n.m.r. spectrum was identical in the 9.0–10.0 τ region with the very complex (approximately 24 peaks) pattern given by authentic tricyclopropylcarbinol. There were no n.m.r. bands, even in the crude hydrolysis product, in the 4.95 (vinyl), 7.47 (allyl), or 5.80 τ $-CH_2OC(=O)-$ regions.

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

Cationic Cyclizations Involving Olefinic Bonds. II.[1] Solvolysis of 5-Hexenyl and *trans*-5,9-Decadienyl *p*-Nitrobenzenesulfonates

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Solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in 98% formic acid containing sodium formate proceeds with participation of the olefinic bond at a rate which is about twice that of the formolysis of the hexyl ester. The product, after saponification, consisted of 68% cyclohexanol, 26% hexenol, 5% cyclohexene, and 1% other hydrocarbons. Formolysis of the *p*-nitrobenzenesulfonates of 4-pentenol and 6-heptenol proceeded with negligible double bond participation to give mainly the products of direct substitution. Formolysis of *trans*-5,9-decadienyl *p*-nitrobenzenesulfonate proceeded with rate acceleration and afforded mainly monocyclic products. Some bicyclic materials were produced and these were shown to be *trans*-decalin derivatives. No *cis*-decalin compounds were found. The exclusive formation of *trans*-fused bicyclic materials is of interest in connection with the biosynthesis of cycloisoprenoids.

The acid-catalyzed cyclization of dienes and polyenes generally lacks selectivity because of the indiscriminate generation of cationic sites. We are directing our attention to systems in which such sites can be generated at a specific position and under conditions which are not acidic enough to effect significant competing protonation of the olefinic bonds. Thus our hope is to learn how to realize a considerable degree of structural as well as stereochemical control over cationic cyclizations involving olefinic bonds. These studies may be of significance in connection with the biosynthesis of cycloisoprenoids.

The first paper of this series[1a] describes an example of the intermolecular counterpart of this principle. We have since been exploring the intramolecular re-

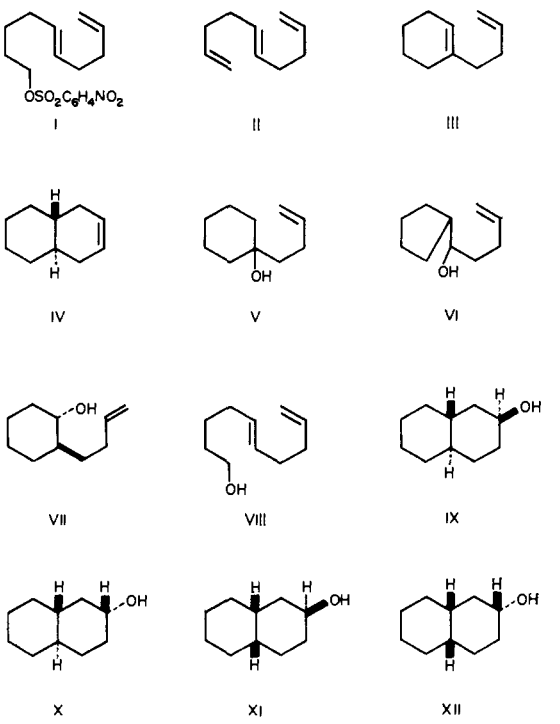
(1) (a) Paper I of this series: W. S. Johnson and R. A. Bell, *Tetrahedron Letters*, **No. 12**, 27 (1960); (b) a preliminary account of the work described in the present paper was reported at the I.U.P.A.C. Meeting in London, July 17, 1963; see W. S. Johnson, *Pure Appl. Chem.*, **7**, 317 (1963).

action, and the present paper discloses some of the results of our studies on the solvolysis of simple olefinic esters.

Bartlett[2] with Clossen has examined the solvolysis of the *p*-nitrobenzenesulfonates of 4-pentenol and 5-hexenol in acetic acid buffered with sodium acetate. They found that, compared with *n*-hexyl *p*-nitrobenzenesulfonate, the former ester showed a slight rate deceleration and yielded only the product of direct substitution; while the latter showed a rate acceleration of about 50% and underwent partial cyclization to give up to 25% yield of cyclohexyl acetate, the balance of the product being mainly the hexenyl acetate. In view of the fact that formic is more effective than acetic acid in promoting the anchimerically assisted process in the solvolysis of phenylethyl tosylate,[3] it was not surprising that we found a somewhat larger rate (approximately double that of the hexyl ester) accompanied by higher yields of cyclization for the solvolysis of hexenyl *p*-nitrobenzenesulfonate in formic rather than acetic acid. The results are summarized in Table I in the Experimental section. Thus the solvolysis (run a) of a 0.02 *M* solution of 5-hexenyl *p*-nitrobenzenesulfonate, m.p. 38.5–40°, in 100% formic acid containing 2 mole equivalents of sodium formate was 96% complete after 3 hr. at 75°. The product, after saponification, was analyzed quantitatively by vapor phase chromatography over a phenyldiethanolamine succinate column and was shown to contain 51% of cyclohexanol, 24% of hexenol, 4% of cyclohexene, and about 20% of other hydrocarbons, including any 1,5-hexadiene. A somewhat higher yield (68%) of cyclohexanol was obtained when 98% (instead of 100%) formic acid was used (run b). As the solvent was diluted further with water, the yield of direct substitution product was increased at the expense of cyclic product. Thus in formic acid containing 10% water (run c) the yields of cyclohexanol and hexenol were 50 and 35%, respectively, and in 40% water (run d), 30 and 58%, respectively. In 100% formic acid, decreasing the temperature to 50° (run e) served to minimize the formation of spurious hydrocarbons and hence to raise the yield of cyclic product to 68%. Lowering the concentration of formate appeared to improve the ratio of cyclized to uncyclized alcohol only slightly (compare runs g with e and h with a).

Formolysis of 4-pentenyl *p*-nitrobenzenesulfonate, m.p. 46–47°, gave no detectable cyclic product. 6-Heptenyl *p*-nitrobenzenesulfonate, m.p. 46–47°, underwent formolysis at approximately the same rate as the hexyl ester, and the failure of the olefinic bond to participate in the solvolysis was reflected also in the nature of the product which was composed mainly (62% yield) of heptenol. A small amount (about 1%) of cycloheptanol, but no cyclohexylcarbinol, was detected. A substantial hydrocarbon fraction was produced, and this may contain cyclized olefins, but the matter has not yet been resolved.

As in the comparable acetolysis experiment,[2] formolysis of the hexenyl ester in the absence of sodium formate gave a mixture containing considerable undesirable material arising from the addition of solvent to the olefinic bond. This process is obviously promoted by protonation of the olefinic bond by the strong acid (*p*-nitrobenzenesulfonic acid) liberated in the reaction. For our further studies, therefore, we considered it desirable to use the buffered medium.



Our attention was next turned to the solvolysis of *trans*-5,9-decadienyl *p*-nitrobenzenesulfonate (I). This substance was prepared by the condensation of 1,4-bromochlorobutane with the monosodio derivative of 1,5-hexadiyne to give 1-chloro-5,9-decadiyne which was converted, by treatment with potassium acetate in dimethylformamide, into the 1-acetoxydecadiyne, and this in turn was saponified to yield the corresponding alcohol. Reduction of the tetrahydropyranyl ether of the diynol with sodium in liquid ammonia under appropriate conditions (see Experimental) afforded, after hydrolysis, the *trans*-dienol which was converted, on treatment with *p*-nitrobenzenesulfonyl chloride and base, into the crystalline *p*-nitrobenzenesulfonate (I), m.p. 40–42°. The solvolysis of a 0.02 *M* solution of the ester I in 80% formic acid containing 2 mole equivalents of sodium formate was ascertained by ultraviolet spectroscopy to be 96% complete after 1 hr. at 75°. It is noteworthy that this reaction is slightly faster than the solvolysis of the hexenyl ester already discussed, which was only 74% completed under identical conditions. This behavior may be a reflection of the stronger nucleophilicity of the internal olefinic bond.

The products of the solvolysis experiments, after hydrolysis with alkali, were analyzed by vapor phase chromatography over a Craig succinate column and compared by peak enhancement with authentic substances. In a typical run the absolute yields of products (with retention times at 157°) were: trace of triene II (2.3 min.), 5.4% of monocyclic diene III (3.1 min.), 2.9% of *trans*-Δ^2-octalin (IV) (4.0 min.), 1.6% of monocyclic tertiary carbinol V (16.6 min.), 14% of a fraction

(2) P. D. Bartlett, *Ann. Chem.*, **653**, 45 (1962); see this paper also for review of previous work.

(3) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

consisting mainly of the product VI of five-membered ring cyclization (18.8 min.), 51.2% of the monocyclic secondary alcohol VII (22.7 min.), 3.3% of the decadienol VIII (26.2 min.), 2.2% of *trans-anti*[4]-2-decalol (IX) (31.4 min.), and 6.7% of *trans-syn*[4]-2-decalol (X) (36.4 min.). In addition, a total of 3.3% of unidentified hydrocarbon fractions (not *cis*-Δ^1- or Δ^2-octalin) was detected (retention times, 2.7 and 4.3 min.). No detectable amounts of *cis-anti*[4]-2-decalol (XI) (46.5 min.) or *cis-syn*[4]-2-decalol (XII) (48.9 min.) were found. The identity of the alcohols V, VI, VII, VIII, IX, and X was confirmed by isolation of the appropriate fractions by preparative vapor phase chromatography and comparison of the infrared spectra with those of authentic specimens. The hitherto unknown Δ^3-butenylcyclopentylcarbinol (VI) was prepared by the reaction of Δ^3-butenylmagnesium bromide with cyclopentanecarboxaldehyde.

Despite the low yield of bicyclic material, it is encouraging to note that the monocyclic alcohol VII represents a relatively large proportion (about 50%) of the solvolysis product. It might be anticipated, therefore, that yields of bicyclic material could be improved by decreasing the nucleophilicity of the solvent which is responsible for the interruption of cyclization at the monocyclic stage. The situation might also be improved by increasing the nucleophilicity of the terminal olefinic bond with an appropriate substituent, *e.g.*, a methyl group at C-9, and we are examining this case. The simple unsubstituted system, indeed, probably represents one of the most unsatisfactory substrates imaginable. It is accordingly a good case for discovering the kinds of side reactions to be dealt with and for determining what kinds of external factors favor cyclization.

The formation of Δ^3-butenylcyclopentylcarbinol (VI) in about 8% yield deserves special comment since it represents cyclization to form a five-membered ring, in contrast with the course of the solvolysis of 4-pentenyl and 5-hexenyl *p*-nitrobenzenesulfonates (see above). The failure in the latter case to observe five-membered ring cyclization may be attributed to the relative instability of the (primary) cyclopentylcarbonium ion that would be involved. It is to be expected, therefore, that the 5-heptenyl derivative, on solvolysis, will yield some product of five-membered ring cyclization. The resistance of 4-pentenyl *p*-nitrobenzenesulfonate to cyclization may be attributable to one or both of the following features: (a) the olefinic bond (at 4,5) is in a less favorable position (compared with 5,6) for overlap of the π-electrons with the incipient cationic site; (b) the cyclopentyl cation that would be formed is probably destabilized owing to the constraint of the preferred 120° angle, relative to an alkylcyclopentyl carbonium ion in which an exocyclic (rather than endocyclic) cationic site is developed. Support for this view is afforded by the solvolysis of 5-isooctenyl tosylate which can give the relatively stable (tertiary) cyclopentyldimethyl carbonium ion and accordingly yield mainly products of five-membered ring closure.[5] We plan to examine the solvolysis of 4-methyl-4-pentenyl *p*-nitrobenzenesulfonate to see if the development of a cyclic tertiary cation can overcome the intrinsic features that oppose cyclization in such a system.

The most significant feature of the solvolysis of I is that the bicyclic product consisted *exclusively* of *trans*-fused material. Since it is known that mineral acid-catalyzed cyclization of the diene III proceeds stereoselectively, although not in good yield, to give the *cis*-fused substance XII,[6,7] the exclusive formation of *trans*-fused product in the present study must occur by a different mechanism, which may have some relationship to the process involved in the biosynthesis of cycloisoprenoids from open-chain polyenes.[8]

As compared with formolysis, solvolysis of the decadienyl *p*-nitrobenzenesulfonate (I) in 100% acetic acid containing sodium acetate expectedly (see above) gave a higher proportion of product VIII (30% yield) of direct substitution at the expense of monocyclic alcohol VII (31% yield). Surprisingly the yield of decalol X (7.6%) was not lowered. Solvolysis in 50% formic acid also had the effect of increasing the amount of the product (VIII) of direct substitution to 14% yield. It was hoped that in this highly aqueous medium, in which the substrate is not completely soluble, there might be a relatively high population of intramolecularly self-solvated, helically conformed molecules[9] in which the double bonds are juxtaposed for ring closure. The failure to observe an increased yield of decalol X, however, suggests that the desired conditions were not realized. When solvolysis was carried out on the adsorbed surface of alumina following the method of Herz and Caple,[10] no cyclization occurred; only the product VIII of direct substitution was found.

In some of our preliminary experiments on the solvolysis of decadienyl *p*-nitrobenzenesulfonate (I), small yields of the *cis*-2-decalols XI and XII were found. At first we entertained the hypothesis that these substances were arising from acid-catalyzed cyclization of the monocyclic diene III as in Linstead's case.[6] However, treatment of the diene III or the tertiary carbinol V under the conditions of our solvolysis experiments gave none of the *cis*-decalols even after prolonged heating. It was finally discovered that the *cis*-decalols were produced only on solvolysis of samples of decadienyl *p*-nitrobenzenesulfonate that were prepared in a particular way (see Experimental) and apparently contained some contaminant, the conversion of which to bicyclic material must be fairly efficient. This matter is being further investigated.

Experimental

Preparation of Materials. 4-Pentenyl *p*-Nitrobenzenesulfonate.—Since preliminary experiments indicated that the conventional sulfonyl chloride–pyridine method of esterification was attended by considerable formation of pyridinium salt, the alkoxide procedure of Kochi and Hammond[11] was used. To a solution

(4) The terms *syn* and *anti* are used here to designate the stereochemical relationship between the hydrogen atoms attached to the carbon bearing the hydroxyl group and to the nearest angular position.

(5) Unpublished observation of E. J. Corey and C. Sauers. We wish to thank Prof. Corey for disclosing this information.

(6) R. P. Linstead, A. B. L. Wang, J. H. Williams, and K. D. Errington, *J. Chem. Soc.*, 1136 (1937).

(7) W. S. Johnson, S. L. Gray, J. K. Crandall, and D. M. Bailey, *J. Am. Chem. Soc.*, **86**, 1966 (1964).

(8) *Cf.*, for example, G. Stork and A. W. Burgstahler, *ibid.*, **77**, 5068 (1955), and A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955). Note, however, that a free-radical mechanism is a possible alternative; R. Breslow, E. Barrett, and E. Mohacsi, *Tetrahedron Letters*, 1207 (1962).

(9) *Cf.* E. E. van Tamelen and T. J. Curphey, *ibid.*, 121 (1962).

(10) W. Herz and G. Caple, *J. Am. Chem. Soc.*, **84**, 3517 (1962).

(11) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3443 (1953).

of 2.15 g. of 4-pentenol[12] in 50 ml. of anhydrous ether was added 0.65 g. of oil-dispersed sodium hydride. The mixture was heated for 12 hr. with stirring (in the presence of several small glass beads to assist in pulverizing the solid phase). The mixture was cooled with an ice–acetone bath; then a solution of 5.6 g. of *p*-nitrobenzenesulfonyl chloride, m.p. 75–76°, in 20 ml. of anhydrous ether was added dropwise over a period of 10 min. After the addition was complete, the mixture was allowed to warm to room temperature and to stir for an additional hour. The precipitated salts were removed by filtration, and the filtrate was evaporated at reduced pressure. Crystallization of the residue from ether–petroleum ether gave 5.8 g. of pale yellow plates, m.p. 45–46°. Repeated recrystallizations from the same solvent system afforded a total of 3.5 g. (52% yield) of material, m.p. 46–47°, which was used in the solvolysis experiments.

Anal. Calcd. for $C_{11}H_{13}O_5NS$: C, 48.70; H, 4.83; N, 5.16; S, 11.80. Found: C, 48.95; H, 5.0; N, 5.1; S, 11.8.

5-Hexenyl *p*-Nitrobenzenesulfonate.—A 5.0-g. sample of 5-hexenol[13] (Peninsular ChemResearch, Inc.) in 50 ml. of anhydrous ether was treated with 1.26 g. of sodium hydride, then with 11.1 g. of *p*-nitrobenzenesulfonyl chloride in 50 ml. of ether as described above for the lower homolog. Crystallization of the crude product from ether–petroleum ether afforded 7.0 g. (first crop) of pale yellow plates, m.p. 38.5–40°, and 1.6 g. (second crop), m.p. 38–39°. Repeated recrystallizations from the same solvent pair afforded material, m.p. 39–40°, $\lambda_{max}^{95\%\ EtOH}$ 250 mμ (ε 11,800).

Anal. Calcd. for $C_{12}H_{15}O_5NS$: C, 50.52; H, 5.30; N, 4.91; S, 11.24. Found: C, 50.7; H, 5.5; N, 5.2; S, 11.2.

***n*-Hexyl *p*-Nitrobenzenesulfonate.**—A 3.15-g. sample of 1-hexanol[14] was treated with sodium hydride and *p*-nitrobenzenesulfonyl chloride as described above for 4-pentenol. Crystallization of the crude product from ether–petroleum ether gave 5.5 g. (first crop), m.p. 49–50°, and 1.1 g. (second crop), m.p. 46–48°. Repeated recrystallizations from the same solvent pair gave pale yellow plates, m.p. 49–50°, $\lambda_{max}^{95\%\ EtOH}$ 250 mμ.

Anal. Calcd. for $C_{12}H_{17}O_5NS$: C, 50.16; H, 5.96; N, 4.88; S, 11.16. Found: C, 50.1; H, 5.9; N, 5.0; S, 11.3.

6-Heptynol.—A mixture of 250 ml. of dimethylformamide, 18.9 g. of 7-chloro-1-heptyne,[15] b.p. 95–96° (60 mm.), and 35 g. of anhydrous potassium acetate was heated at 85° for 54 hr. The mixture was cooled, diluted with water, and extracted thoroughly with ether. The combined organic layers were washed thoroughly with water. The residue obtained upon distillation of the solvent was heated under reflux with 400 ml. of 0.75 *N* sodium hydroxide in 50% aqueous ethanol for 2 hr. The mixture was extracted with ether, and the combined organic layers were washed with water, then with saturated brine, and dried over anhydrous sodium sulfate. Distillation through a 2-ft. Podbielniak-type column afforded 11.7 g. (72% yield) of 6-heptynol, b.p. 115–116° (49 mm.), $n^{25}D$ 1.4511 (reported[15] 98° (20 mm.), $n^{25}D$ 1.4534). Vapor phase chromatography on a 15% phenyldiethanolamine succinate column indicated that this product was 99% pure.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.0; H, 10.7.

6-Heptenol was prepared from the aforementioned 6-heptynol according to a previously described general procedure.[16] The product, on distillation through a 12-in. micro-Podbielniak-type column, was obtained in 75% yield as a colorless liquid, b.p. 112–113° (69 mm.), $n^{26}D$ 1.4381 (reported[17] 88° (20 mm.), $n^{20}D$ 1.4440). Vapor phase chromatography on a 15% phenyldiethanolamine succinate column showed response for approximately 2% of a second component identified as 1-heptanol by peak enhancement with authentic material.

6-Heptenyl *p*-Nitrobenzenesulfonate.—A 1.43-g. specimen of 6-heptenol, prepared as described in the preceding experiment, was treated with sodium hydride and *p*-nitrobenzenesulfonyl chloride as described above for 4-pentenol. The crude product on crystallization from ether–petroleum ether gave a total of 2.1 g. (56% yield) of the ester, m.p. 46–47°. Repeated recrystallizations from ether–petroleum ether gave pale yellow plates, m.p. 46.5–47.5°, $\lambda_{max}^{95\%\ EtOH}$ 250 mμ (ε 11,700).

Anal. Calcd. for $C_{13}H_{17}O_5NS$: C, 52.16; H, 5.73; N, 4.68; S, 10.71. Found: C, 52.1; H, 5.9; N, 4.8; S, 11.0.

1-Chloro-5,9-decadiyne.—The monosodio derivative of 1,5-hexadiyne was prepared according to the procedure of Raphael and Sondheimer.[18] Thus 45.0 g. of the diyne,[18] b.p. 87–88° (760 mm.), was added to a suspension of sodamide (from 12.7 g. of sodium) in 1 l. of liquid ammonia. The mixture was stirred under reflux for 2.5 hr.; then 103 g. of 1-bromo-4-chlorobutane,[15] b.p. 72–78° (18–22 mm.), was added over a 5-min. period. The last of the halide was washed in with a little anhydrous ether. The mixture was stirred under reflux for 3.5 hr.; then 500 ml. of anhydrous ether was added, and the ammonia allowed to evaporate overnight. The residue was diluted with water, and the organic layer was washed in turn with water, 5% hydrochloric acid, 5% potassium carbonate solution, again with water, followed by saturated brine, and finally dried over anhydrous sodium sulfate. The oily residue obtained on evaporation of the solvent under reduced pressure was distilled through a 6-in. Vigreux column to give 43.3 g. (47% yield) of chlorodiyne as a colorless oil, b.p. 65–66° (0.3 mm.), $n^{22}D$ 1.4834.

Anal. Calcd. for $C_{10}H_{13}Cl$: C, 71.20; H, 7.78; Cl, 21.02. Found: C, 70.85; H, 7.8; Cl, 20.75.

5,9-Decadiynol.—A mixture of 43.3 g. of 1-chloro-5,9-decadiyne,[18] b.p. 65–66° (0.3 mm.), $n^{25}D$ 1.4834, 50 g. of anhydrous potassium acetate, and 1 l. of dimethylformamide was heated under reflux with stirring in an atmosphere of nitrogen for 24 hr. The mixture was then cooled and filtered, and the precipitated salts were washed with benzene. The combined filtrates and washings were concentrated under reduced pressure to a volume of approximately 350 ml. This solution was added to 1.5 l. of water and extracted thoroughly with petroleum ether. The combined organic layers were washed thoroughly with water and then evaporated under reduced pressure to give 49 g. of crude acetate. Comparable material from another experiment on a smaller scale was evaporatively distilled at 105° (0.15 mm.) to give **5,9-decadiynyl acetate** as a colorless oil, λ_{max}^{film} 3.0 μ (C≡CH), 4.7 (C≡C), 5.75 (C=O), and 8.1 (acetate C—O).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.7; H, 8.3.

The 49 g. of crude acetate was dissolved in 200 ml. of absolute ethanol and 300 ml. of 1.5 *N* aqueous sodium hydroxide, and the mixture was heated under reflux in an atmosphere of nitrogen for 1 hr. The mixture was then cooled, diluted with water, and extracted thoroughly with ether. The combined organic layers were washed with saturated brine and dried over anhydrous sodium sulfate. The pale brown oily residue obtained on evaporation of the solvent under reduced pressure amounted to 34.9 g. of crude diynol. A sample of this material was evaporatively distilled at 110° (0.3 mm.), λ_{max}^{film} 2.8–3.0 μ (OH, C≡CH) and 4.7 (C≡C).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.8; H, 9.7.

***trans*-5,9-Decadienol (VIII).**—The conversion of 5,9-decadiynol to pure *trans*-5,9-decadienol presented some problems. Dialkylacetylenic bonds are reduced with sodium and liquid ammonia stereospecifically to *trans*-olefins only in the absence of acidic proton donors like ammonium sulfate.[16] Terminal acetylenic bonds, on the other hand, are incompletely reduced in the absence of such proton donors. Since the terminal acetylenic residue can be protected against reduction by conversion to the anion, as demonstrated by the successful reduction of undeca-1,7-diyne to undeca-7(*trans*)-en-1-yne,[19] we explored the stepwise procedure involving treatment of the diynol with sodium amide in liquid ammonia. However, when this was followed by treatment with sodium, reduction of the internal acetylenic bond was

(12) This material was prepared from 4-pentynol (G. Eglinton, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2879 (1952)) by reduction with sodium in liquid ammonia according to the general procedure of A. L. Henne and K. W. Greenlee, *J. Am. Chem. Soc.*, **65**, 2020 (1943). The product, on distillation through a 24-in. Podbielniak-type column, was obtained in 80% yield, b.p. 84–85° (90 mm.), $n^{20}D$ 1.4548. Vapor phase chromatography on a 15% Craig succinate column at 130° (flow rate 27 ml./min.) showed two components: 96% of 4-pentenol (retention time 6.2 min.) and 4% of 1-pentanol (retention time 4.75 min.).

(13) Vapor phase chromatography on a 15% phenyldiethanolamine succinate column at 100° at a gas flow rate of 25 ml./min. gave response for only one component (retention time 11.8 min.).

(14) Commercial 1-hexanol was distilled from calcium hydride. Vapor phase chromatography on a 15% Craig succinate column at 132° and a flow rate of 25 ml./min. gave response for two components: 98% of 1-hexanol (retention time 4.8 min.) and 2% of unidentified material (4.1 min.).

(15) M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).

(16) A. L. Henne and K. W. Greenlee, *ibid.*, **65**, 2020 (1943).

(17) T. D. Perrine, *J. Org. Chem.*, **18**, 1361 (1953).

(18) R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 120 (1950).

(19) R. A. Raphael in "Acetylenic Compounds in Organic Synthesis," Academic Press, Inc., New York, N. Y., 1955, p. 201.

incomplete, perhaps due to insolubility of the dianion. We therefore prepared the tetrahydropyranyl ether, and the reduction proceeded satisfactorily. Without isolation, just enough ammonium chloride was added to the reaction mixture to liberate the enyne *in situ;* then excess ammonium sulfate[20] was added as a proton source, followed by more sodium to effect complete reduction of the terminal acetylenic bond. After acid hydrolysis of the ether group, the desired *trans*-dienol was isolated.

The purest specimens of *trans*-dienol were obtained when the anion was produced by the addition of methyllithium to a solution of the diyne tetrahydropyranyl ether in liquid ammonia, and this procedure is described in detail below. The sodium amide method resulted in products which yielded some *cis*-decalin derivatives in the solvolysis experiments.

A solution of 10.75 g. of the crude 5,9-decadiynol described in the preceding experiment in 15 ml. of dihydropyran was treated with 3 drops of phosphorus oxychloride. The mixture, which had initially become warm due to an exothermic reaction, was allowed to stand at 26° for 24 hr. Ether was then added, and the solution was washed thoroughly with 5% aqueous potassium carbonate and dried over anhydrous sodium sulfate. The crude tetrahydropyranyl ether obtained on evaporation of the solvent at reduced pressure was dissolved in 200 ml. of anhydrous ether; then 200 ml. of a 0.43 *N* solution of methyllithium in ether was added with stirring under anhydrous conditions. The mixture was allowed to stir for 30 min. at 27°, and then approximately 300 ml. of ether was removed by distillation. Anhydrous ammonia (500 ml.) was added to the residue, followed by a total of 3.98 g. of sodium metal which was introduced in small pieces so as to allow for complete reaction of each portion. After the addition was complete (1 hr.), 13.8 g. of ammonium chloride was added, followed (after 15 min.) by 19.4 g. of finely powdered ammonium sulfate. An additional 3.98 g. of sodium was added in pieces as before. Finally, after a stirring period of 1.5 hr., an additional 3.5 g. of ammonium sulfate was introduced, and the ammonia was then allowed to evaporate. The residue was diluted with water and extracted with ether. The organic layers were then washed with water, followed by saturated brine, and dried over anhydrous sodium sulfate. The pale yellow oily residue obtained on evaporation of the ether was dissolved in 100 ml. of absolute ethanol containing 100 mg. of *p*-toluenesulfonic acid monohydrate and heated under reflux in an atmosphere of nitrogen for 3.5 hr. The mixture was cooled, diluted with water, and extracted with benzene. The organic layers were washed with water, followed by saturated brine, and dried over anhydrous sodium sulfate. The residue obtained on evaporation of the solvent at reduced pressure was distilled through a 6-in. Vigreux column to give 8.0 g. (73% over-all yield) of a colorless liquid, b.p. 47–49° (0.03 mm.), $n^{26}D$ 1.4615; λ_{max}^{film} 3.0 μ, broad (OH), 6.1 (C=C), 10.1 and 10.92 (CH=CH_2), and 10.3 (*trans*-CH=CH).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.7; H, 11.7.

***trans*-5,9-Decadienyl *p*-Nitrobenzenesulfonate** (I).—A suspension of 1.70 g. of *trans*-5,9-decadienol, b.p. 47–49° (0.03 mm.), prepared as described in the preceding experiment, in 25 ml. of 30% aqueous potassium hydroxide was cooled with an ice–salt bath and stirred rapidly (Hershberg stirrer) while a solution of 2.72 g. of *p*-nitrobenzenesulfonyl chloride, m.p. 75–77°, in 7 ml. of tetrahydropyran was added over a 15-min. period. Stirring was continued with cooling for an additional 30 min.; then the mixture was diluted with water and extracted with ether. The organic layers were washed with water, followed by saturated brine, and dried over anhydrous sodium sulfate. The residue obtained on evaporation of the solvent was chromatographed on 100 g. of acid-washed alumina (Merck and Co., Inc.). The fraction eluted with 10% ether in petroleum ether amounted to 1.16 g. of oily crystals. Crystallization from pentane gave 0.79 g. (21% yield) of ivory-colored plates, m.p. 40–42°, $\lambda_{max}^{95\%\ EtOH}$ 251 mμ (ϵ 11,700).

Anal. Calcd. for $C_{16}H_{21}O_5NS$: C, 56.62; H, 6.24; N, 4.13. Found: C, 56.7; H, 6.2; N, 4.3.

A better yield of this ester I was obtained as follows. To an ice-cold solution of 0.50 g. of the decadienol in 5 ml. of anhydrous pyridine was added 0.72 g. of *p*-nitrobenzenesulfonyl chloride. The mixture was swirled at −15° for 3 hr., and then diluted with ice–water containing 5 ml. of concentrated hydrochloric acid. The yellow crystals were separated by filtration, dried, and recrystallized from 60–68° petroleum ether to give 0.54 g. (49% yield) of product, m.p. 40–41°.

***trans*-2-(Δ^3-Butenyl)cyclohexanol** (VII).—A solution of 7.0 g. of 2-(Δ^3-butenyl)cyclohexanone,[21] b.p. 104–107° (17 mm.), in 125 ml. of absolute ethanol was stirred and heated under reflux while 11.0 g. of sodium metal was added in small pieces through the condenser. Each piece of sodium was allowed to react completely before addition of the next portion. After all of the metal had reacted, the mixture was cooled, diluted with water, and extracted with ether. The organic layers were washed with water, followed by saturated brine, and dried over anhydrous sodium sulfate. The residue obtained on evaporation of the solvent was dissolved in 100 ml. of anhydrous pyridine, and, while stirring and cooling (ice bath), 11.4 g. of 3,5-dinitrobenzoyl chloride, m.p. 68–69°, was added. After 15 min. the cooling bath was removed, and stirring was continued for 1 hr. at room temperature. The solution was again cooled (ice bath), 25 ml. of water was added, and stirring was continued for an additional hr. The mixture was diluted with ether, then washed with water, cold 5% hydrochloric acid, 5% sodium bicarbonate, again with water, and finally with saturated brine. The solution was dried over anhydrous sodium sulfate, and the solvent was removed by evaporation under reduced pressure. The residue was quickly chromatographed on 150 g. of Florisil, and the fraction eluted with petroleum ether through 40% benzene in petroleum ether was crystallized from petroleum ether to give 7.4 g. (47% yield) of yellow flakes, m.p. 60–63°. Two more recrystallizations from the same solvent gave 6.6 g. (42% yield) of *trans*-2-(Δ^3-**butenyl)cyclohexyl 3,5-dinitrobenzoate** as pale yellow flakes, m.p. 64–65.5° (in an evacuated capillary).

Anal. Calcd. for $C_{17}H_{20}O_6N_2$: C, 58.61; H, 5.79. Found: C, 58.5; H, 5.9.

A solution of the aforementioned 6.6 g. of dinitrobenzoate in 25 ml. of 95% ethanol and 25 ml. of 10% aqueous sodium hydroxide was heated under reflux in an atmosphere of nitrogen for 1 hr. The mixture was then cooled, diluted with water, and extracted thoroughly with benzene. The combined organic layers were washed thoroughly with water until the aqueous layer was colorless and then dried over anhydrous sodium sulfate. The residue obtained on evaporation of the solvent under reduced pressure was distilled through a short Claisen head to give 2.2 g. (74% yield) of colorless liquid, b.p. 76–77° (2 mm.), $n^{25}D$ 1.4761.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.5; H, 11.6.

Δ^3-Butenylcyclopentylcarbinol (VI).—Δ^3-Butenylmagnesium bromide was prepared by adding a solution of 2.2 g. of 4-bromo-1-butene[21] in 5 ml. of anhydrous tetrahydrofuran to 250 mg. of magnesium turnings in 15 ml. of tetrahydrofuran under a nitrogen atmosphere. After reaction commenced, the mixture was stirred for 6 hr. at room temperature; then a solution of 0.50 g. of cyclopentanecarboxaldehyde[22] in 1 ml. of anhydrous ether was added. The mixture was stirred overnight at room temperature; then saturated aqueous ammonium chloride solution was added, and the aqueous layer was extracted with ether. The combined organic layers were washed with saturated sodium bicarbonate solution, followed by saturated brine, and finally dried over anhydrous magnesium sulfate. The residue obtained on removal of the solvent by distillation through a short Vigreux column was purified by preparative vapor phase chromatography on the column described above. The yield was 0.56 g. of colorless liquid, $n^{22}D$ 1.4776 ; λ_{max}^{film} 2.95, 3.22, 6.07, 10.03, and 10.93 μ.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.7; H, 11.8.

The n.m.r. spectrum was determined under the supervision of Dr. L. J. Durham on a Varian Associates A-60 n.m.r. spectrometer. Deuteriochloroform was employed as the solvent with tetramethylsilane as the internal reference. The spectrum exhibited absorption for 1 proton as a characteristic (11 visible peaks) multiplet at δ 5.5–6.3 p.p.m. (penultimate vinyl proton), 2 protons as a triplet at 4.8–5.3 (terminal vinyl protons), 1 proton

(20) The use of the more soluble ammonium chloride as a proton source results in over-reduction; ref. 16.

(21) D. C. Hibbit and R. P. Linstead, *J. Chem. Soc.*, 470 (1936). Note that the 4-bromo-1-butene was prepared from the alcohol according to the procedure of F. B. LaForge, N. Green, and W. A. Gersdorff, *J. Am. Chem. Soc.*, **70**, 3707 (1948), for the preparation of 5-bromo-1-pentene.

(22) Prepared essentially by the method of R. Roth and H. Erlenmeyer, *Helv. Chim. Acta*, **38**, 1276 (1955), and finally purified by preparative vapor phase chromatography on a 20-ft. × 3/8-in. column packed with 20% Carbowax 20M.

TABLE I

FORMOLYSIS OF 5-HEXENYL *p*-NITROBENZENESULFONATE

Run	% H_2O	Molar concn. of substrate	Molar concn. of HCOONa	Temp., °C.	Time, hr.	Reaction, %	Yield, % 5-Hexenol	Yield, % Cyclohexanol	Yield, % Cyclohexene	Yield, % Other hydrocarbons (including 1,5-hexadiene)
a	0	0.02	0.04	75	3	96	24	51	4	*Ca.* 20
b	2	.02	.04	75	3	96	26	68	5	*Ca.* 2
c	10	.02	.04	75	3	93	35	50	6	*Ca.* 7
d	40	.02	.04	75	3	95	59	30	1	*Ca.* 3
e	0	.02	.04	50	23	91	27	68	1	*Ca.* 3
f	0	.01	.02	50	23	90	28	69	2	...
g	0	.005	.01	50	23	90	23	65	1	...
h	0	.01	.02	75	3	94	23	60	2	...
i	0	.02	.04	100	0.3	96	20	53	3	...
j	2	.005	.01	50	23	89	28	63	...	...

as a multiplet centered at 3.41 (proton on carbon holding hydroxyl group), 1 proton as a sharp singlet at 2.28 (OH), and 13 protons as an unresolved signal at 1.0–2.5.

trans-**1,5,9-Decatriene** (II) was prepared by the method of Sondheimer and Gaoni[23] but prior to their publication. Thus we obtained material in 44% yield, b.p. 64–65° (20 mm.), $n^{22}D$ 1.4458 (reported[23] 69–70° (18 mm.), $n^{25}D$ 1.4447).

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.0; H, 11.8.

trans-**Δ^2-Octalin** (IV) was prepared by a previously described procedure.[24] Even though the hydrocarbon was regenerated from "pure" dibromide, m.p. 84–85°, vapor phase chromatographic analysis indicated that it contained 8% impurity (possibly *cis*-Δ^2-octalin).

1-**Δ^3-Butenylcyclohexene** (III) was prepared as previously described.[6] Vapor phase chromatographic analysis of our sample indicated no detectable impurity.

1-**Δ^3-Butenylcyclohexanol** (V) was prepared as previously described.[6] Vapor phase chromatographic analysis indicated the presence of about 2% of a contaminant.

Cyclization Studies. 5-Hexenyl *p*-Nitrobenzenesulfonate.—The following constitutes a detailed description of run a of the formolysis of this ester as summarized in Table I. The other runs b–j were conducted in an identical fashion except for the differences summarized in the table.

To 53 ml. of anhydrous[25] formic acid preheated to 75° was added 0.302 g. of 5-hexenyl *p*-nitrobenzenesulfonate, m.p. 39–40°, and 0.144 g. of anhydrous sodium formate. The solution was heated under an atmosphere of nitrogen in a bath maintained at 75 ± 2°. The reaction mixture was then rapidly cooled and divided into two exactly equal parts. Each was separately neutralized with 79 ml. of 30% aqueous sodium hydroxide. (Control experiments indicated that formates were completely cleaved under these conditions.) One of the portions was saturated with potassium carbonate and extracted thoroughly with ether. The organic layers were washed with saturated brine, dried over anhydrous sodium sulfate, and diluted to exactly 50 ml. with ether for analysis of the alcoholic products.

The other portion of the mixture was extracted with 20 ml. of methylcyclohexane in five portions. The organic layers were washed with saturated brine and distilled into a 25-ml. volumetric flask, then diluted to exactly 25 ml. with methylcyclohexane. This sample was used for analysis of hydrocarbons as described below.

A 1-ml. aliquot of the 50-ml. ether solution was evaporated and diluted to 5 ml. with 95% ethanol. The ultraviolet absorption spectrum of this solution was determined, λ_{max} 250 mμ (ϵ 440), corresponding to a yield of 4% of unreacted *p*-nitrobenzenesulfonate. The solvolysis, therefore, was approximately 96% complete.

The formolysis products in the 50-ml. ether solution were analyzed for alcohols on an Aerograph (A-550) gas chromatograph equipped with a hydrogen flame ionizer detector and a 5-ft. × 1/8-in. 15% phenyldiethanolamine succinate column operated at 113° with nitrogen and hydrogen flow rates of 25 ml./min. The products were identified by peak enhancements with authentic samples of 5-hexenol (retention time 8.4 min.) and cyclohexanol (9.9 min.). Confirmation of the identity of cyclohexanol was obtained by isolation from a similar experiment (in 98% formic acid) by distillation. The product was treated with phenyl isocyanate and, after three recrystallizations from petroleum ether, the phenylurethan was obtained as colorless crystals, m.p. 81.5–82.5°, alone or on admixture with an authentic specimen. The absolute yields of 5-hexenol and cyclohexanol in the solvolysis experiment were determined by adding 1 ml. of a standard (3.72×10^{-2} *M*) solution of 6-heptenol and 1 ml. of a standard (4.48×10^{-2} *M*) solution of cyclohexylcarbinol to a 5-ml. aliquot of the 50-ml. ether solution. The relative peak areas, determined by planimetry, were: 5-hexenol, 0.120 (retention time 8.4 min.); cyclohexanol, 0.310 (9.9 min.); 6-heptenol, 0.430 (14 min.); and cyclohexylcarbinol, 0.560 (19.6 min.). These values were then corrected for relative detector response (0.84:1:1:1, respectively) which was obtained from mixtures of known concentrations of the four components. The product composition of the alcohols in the solvolysis mixture was calculated to be 32% 5-hexenol and 68% cyclohexanol. The combined concentration of the two alcohols was calculated to be 7.6×10^{-3} *M*, corresponding to an absolute yield (corrected for unreacted *p*-nitrobenzenesulfonate) of 75%, or 51% cyclohexanol and 24% 5-hexenol. Another determination employing 1 ml. each of the standard solutions and 8 ml. of the ether solution of formolysis products gave identical results.

The 25-ml. methylcyclohexane solution was analyzed for hydrocarbons by vapor phase chromatography (see above) over a 5-ft. × 1/8-in. 20% SE 30 silicone-rubber column operated at 48°. The major fraction (91%) was obtained as a multiplet of peaks (retention time 4–6 min.) and, as shown be peak enhancement experiments, included any 1,5-hexadiene (4 min.). The remaining fraction (9%) corresponded to cyclohexene (8 min.) as indicated by peak enhancement with authentic material. An approximate absolute yield of cyclohexene was determined by vapor phase chromatographic analysis of a 10-ml. aliquot of the methylcyclohexane solution containing exactly 6 mg. of added cyclohexene. The relative peak areas of the unidentified hydrocarbon fraction (including 1,5-hexadiene) and the cyclohexene fraction were 1:1.01. The concentration of cyclohexene, therefore, was approximately 8×10^{-4} *M*, corresponding to a 4% yield. In other solvolysis experiments where the yield of the unidentified hydrocarbons was low relative to cyclohexene, 1,5-hexadiene was used instead of cyclohexene as the standard for determination of absolute yield.

6-Heptenyl *p*-Nitrobenzenesulfonate.—To 41.5 ml. of anhydrous[25] formic acid preheated to 75° was added 0.249 g. of 6-heptenyl *p*-nitrobenzenesulfonate, m.p. 46–47°, and 0.113 g. of anhydrous sodium formate. The solution was heated under nitrogen with a bath maintained at 75 ± 2° for 6 hr. The mixture was rapidly cooled and was divided into two equal parts which were treated exactly as described above for the hexenyl ester except that one of the portions was extracted with carbon disulfide instead of methylcyclohexane for use in the analysis of hydrocarbons.

The extent of solvolysis was determined to be 88% by ultraviolet spectroscopy as described above for the hexenyl ester.

The 50-ml. ether solution of the formolysis products was used for analysis of the alcohols just as described in the preceding experiment except that the column temperature was 112–134°. By peak enhancement experiments with authentic 6-heptenol

(23) F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **84**, 3520 (1962).

(24) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *ibid.*, **83**, 606 (1961).

(25) Prepared by distillation from boric anhydride; see H. I. Schlesinger and A. W. Martin, *ibid.*, **36**, 1589 (1914).

(retention time 9 min. at 134°) and cycloheptanol (14.3 min.), it was apparent that the product consisted principally of the former with only a trace of the latter substance. The yield of 6-heptenol was determined by adding a known amount of cyclohexylcarbinol (retention time 12.8 min. at 134°). Thus the concentration of 6-heptenol was shown to be 4.0×10^{-3} *M*, corresponding to a yield of 66% (corrected for 1-hexanol contaminating the starting material).

The 50-ml. carbon disulfide solution was analyzed for hydrocarbons as described above on the SE 30 silicone-rubber column at 57°. The chromatogram consisted of two unidentified peaks of about equal area: A (retention time 5.5 min.) and B (8.8 min.). An approximate determination of the absolute yield of these hydrocarbons was made using 1-methylcyclohexene (Aldrich Chemical Co.) as a standard and assuming identical detector response. Thus the total yield of these hydrocarbons was approximately 18%.

4-Pentenyl *p*-Nitrobenzenesulfonate.—To 53 ml. of anhydrous[25] formic acid preheated to 75° was added 0.288 g. of 4-pentenyl *p*-nitrobenzenesulfonate, m.p. 46–47°, and 0.144 g. of anhydrous sodium formate. The solution was heated under nitrogen with a bath maintained at 75 ± 2° for 6 hr. The mixture was rapidly cooled and was divided into two equal parts which were treated exactly as described above for the hexenyl ester. The extent of solvolysis was determined as 89% by ultraviolet spectroscopy as described above for the hexenyl ester.

The 50-ml. ether solution of the formolysis products was used for analysis of the alcohols just as described for the hexenyl ester except that the column temperature was 100°. By peak enhancement experiments with authentic samples, it was determined that the product consisted principally of 4-pentenol (retention time 6.5 min.) and pentanol (5.0 min.), which was an impurity in the starting 4-pentenol. The absolute yield of 4-pentenol was determined by adding a known amount of 5-hexenol (retention time 11.8 min. at 100°). Thus the concentration of 4-pentenol was shown to be 8.5×10^{-3} *M*, corresponding to a yield of 90%.

The 25-ml. methylcyclohexane solution was analyzed for hydrocarbons as described above on the SE 30 silicone-rubber column at 55°. No peaks corresponding to hydrocarbons could be detected between retention times of 0 to 6 min. The retention time of authentic cyclopentene (Aldrich Chemical Co.) was 2.4 min. under these conditions.

***trans*-5,9-Decadienyl *p*-Nitrobenzenesulfonate.** (a) **In 80% Formic Acid.**—To 13.3 ml. of a 0.04 *M* solution of sodium formate in 80% formic acid preheated to 75° was added, with stirring, 90 mg. of *trans*-5,9-decadienyl *p*-nitrobenzenesulfonate, m.p. 40–42° The mixture was heated in an atmosphere of nitrogen at 75 ± 2° for 1 hr. The solution was then rapidly cooled with an ice bath and poured into 40 ml. of ice-cold 30% aqueous sodium hydroxide containing ice. Salt was added to the point of saturation, and the mixture was extracted with 45 ml. of ether in five portions. The combined organic layers were dried over anhydrous potassium carbonate and diluted to exactly 50 ml. A 1.0 ml. aliquot was used for determining the extent of reaction (96%) by ultraviolet spectroscopy as described above for the 5-hexenyl ester. The remaining 49 ml. of the ether solution was concentrated nearly to dryness by distillation through a 2-ft. Podbielniak-type column. The residue (about 1 ml.) was diluted to exactly 10 ml. with carbon disulfide, and this solution was used for vapor phase chromatographic analysis over a 7.5-ft. × 1/8-in. column packed with 15% Craig succinate on Chromosorb W at a gas flow rate of 25 ml./min. Temperature settings were in the range 90–110° for olefin analysis and 155–185° for alcohol analysis. Average area measurements obtained (by triangular approximation) from two separate injections were compared with those from two additional injections of mixtures to which an equal amount of a 3.95×10^{-3} *M* solution of authentic *trans-syn*-β-decalol was added. Most of the fractions were identified by peak enhancement experiments with *trans*-1,5,9-decatriene (II; retention time 4.6 min. at 100°), 1-Δ³-butenylcyclohexene (III; 7.3 min., 100°), *trans*-Δ²-octalin (IV; 8.9 min., 100°), 1-Δ³-butenylcyclohexanol (V; 16.6 min., 157°), Δ³-butenylcyclopentylcarbinol (VI; 18.8 min., 157°), *trans*-2-Δ³-butenylcyclohexanol (VII; 22.7 min., 157°), *trans*-5,9-decadienol (VIII; 26.2 min., 157°), *trans-anti*-2-decalol (IX; 31.4 min., 157°), *trans-syn*-2-decalol (X; 36.4 min., 157°), *cis-anti*-2-decalol (XI; 46.5 min., 157°), and *cis-syn*-2-decalol (XII; 49.0 min., 157°). The yields of the alcohols were thus calculated by assuming identical detector response for each. The analysis for olefins was conducted similarly from the data obtained at the lower temperature using a 3.86×10^{-3} *M* solution of *trans*-Δ²-octalin as the standard.

The absolute yields (corrected for the extent of solvolysis) thus calculated for two separate solvolysis runs performed just as described above were: 4.6 and 5.4% of III, 2.5 and 2.9% of IV, 2.5 and 3.3% of total unidentified olefinic peaks (retention times 6.0 and 10.9 min. at 100°), 1.6 and 1.6% of V, 12.1 and 13.9% of a fraction containing Δ³-butenylcyclopentylcarbinol (VI) and a formate (see below; retention time 18.8 min. at 157°), 47.9 and 51.2% of VII, 3.2 and 3.3% of VIII, 2.0 and 2.2% of IX, and 6.2 and 6.7% of X.

Another experiment was carried out on a 2-g. scale. The procedure was essentially the same as that described above except that the crude product obtained after distillation of the solvent was dissolved in 10 ml. of ether and added dropwise with stirring and cooling (ice bath) to a slurry of 0.50 g. of lithium aluminum hydride in 30 ml. of ether. The purpose of this treatment was to ensure cleavage of formate esters, since it was shown that in the experiments described above a portion of the peak corresponding to Δ³-butenylcyclopentylcarbinol (VI) was due to formate. (This may in fact be the formate of VII which has the same retention time as alcohol A.) The lithium aluminum hydride reduction mixture was stirred for 1 hr.; then the excess reagent was decomposed by the dropwise addition of water. Sufficient dilute sulfuric acid was added (in the cold) to dissolve the inorganic salts; then the aqueous layer was extracted with ether. The combined organic layers were washed with saturated sodium bicarbonate solution, then with water, and dried over anhydrous magnesium sulfate. The residue obtained on evaporation of the solvent was submitted to preparative vapor phase chromatography on an Aerograph Autoprep chromatograph equipped with a 20-ft. column of 20% Carbowax 20M. The following alcoholic fractions, corresponding to those described above in the analytical experiment, were collected and their infrared spectra determined. The spectra of the materials regarded by peak enhancement experiments (see above) as V, VI, VII, VIII, IX, and X were shown to be identical with those of the corresponding authentic materials, thus confirming the constitution of the major solvolysis products. The solvolysis mixture from the large-scale experiment was also submitted to quantitative analysis for the alcohols by the method described above, and the following yields were calculated: 2.8% of V, 7.9% of VI, 41.9% of VII, 8.0% of VIII, 2.7% of IX, and 7.4% of X. The significantly lower yield (8%) of VI is presumably due to removal of the formate impurities. The infrared spectrum of Δ³-butenylcyclopentylcarbinol (VI) was the only one of those mentioned above that was not rich in detail in the long wave region. Therefore the n.m.r. spectrum of the solvolysis fraction was obtained and was found to be identical with the highly characteristic spectrum of the authentic material (see above). Moreover, the retention times of the two materials were identical on vapor phase chromatography on two different analytical columns: 15% Carbowax 20M and 20% butanediol succinate.

(b) **In Acetic Acid.**—A (small-scale) solvolysis was conducted as described in part (a) above (the lithium aluminum hydride treatment was included) except that 100% acetic acid containing 2 mole equivalents of sodium acetate was used as the medium, and the heating period was 6 hr. The major difference in the results was that the solvolysis was only 38% complete, and the yields of monocyclic alcohol VII and uncyclized alcohol VIII were 31 and 30%, respectively (corrected for extent of reaction).

(c) **In 50% Formic Acid.**—A solvolysis was conducted as described in part (a) above (the lithium aluminum hydride treatment was included) except that 50 instead of 80% formic acid was employed and the heating period was 6 hr. (reaction 74% complete). The most significant difference in the results was that the yields of VII and VIII were 33 and 14%, respectively.

Relative Rates of Formolysis Reactions.—Since we elected to carry out the solvolysis studies under conditions where the concentration of formate was changing as the reaction proceeded, no attempt was made to obtain precise kinetic data. The relative rate data reported in the discussion part of this paper refer simply to the relative time required for the solvolysis to proceed to the half-way point. The technique employed is described in the experiment detailed below.

To 20 ml. of anhydrous formic acid, preheated to 75 ± 2°, were added 0.054 g. of anhydrous sodium formate and 0.114 g. of 5-hexenyl *p*-nitrobenzenesulfonate. A 1-ml. aliquot was immediately removed, and further 1-ml. aliquots were taken as the

reaction progressed. As soon as removed, these aliquots were cooled in an ice bath, neutralized with 15% aqueous sodium hydroxide, and extracted thoroughly with ether. The combined organic layers were then washed with saturated brine, and the solvent was removed by evaporation under reduced pressure. The residue was then diluted to a known volume with 95% ethanol, and the amount of 5-hexenyl *p*-nitrobenzenesulfonate was determined by ultraviolet spectroscopy. From these data the time required for 50% reaction was determined in this case to be approximately 40 min. In a similar manner the half-lives for the solvolysis of *n*-hexyl and of 6-heptenyl *p*-nitrobenzenesulfonates were found to be 85 and 100 min., respectively. In 80% formic acid the half-lives of 5-hexenyl and of *n*-hexyl *p*-nitrobenzenesulfonates were found to be 30 and 42 min., respectively.

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Cationic Cyclizations Involving Olefinic Bonds. III.[1] On the Mechanism of Formation of *trans*-Fused Rings

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Evidence and arguments have been adduced to support the hypothesis that the 2-Δ^3-butenylcyclohexyl cation (formula D) and related systems will undergo ring closure stereoselectively to form preferentially the *trans*-decalin ring system (formula E). In accordance with this view, the cation D is not involved in the acid-catalyzed cyclization of Δ^3-butenylcyclohexene which, in contrast, gives mainly *cis*-decalin derivatives and is therefore regarded as a concerted protonation–cyclization (Fig. 2). The possible relationship of these considerations to the biosynthesis of polycycloisoprenoids is discussed.

The stereorational theory of Stork[2] and Eschenmoser[3] for the biogenesis of the polycyclotriterpenoids and steroids is based on the premise that the *trans*-fused ring systems are produced by what is in effect a synchronous process[4] initiated by electrophilic attack (*e.g.*, by ^+OH) on an all *trans*-fused polyene as represented in Fig. 1. If the nucleophile Y is an external species, such as the solvent, the cyclization process is interrupted with the formation of two *trans*-fused rings; on the other hand, if Y represents an appropriately juxtaposed olefinic bond in the side chain R, the cyclization process may continue further to give *trans-anti-trans*-fused rings. A corollary to this principle is that a synchronous[4] protonation and cyclization of a monocyclic diene, like Δ^3-butenyl-1-cyclohexene, will produce exclusively a *cis*-fused ring system as depicted in Fig. 2. The cyclization of butenylcyclohexene (Fig. 2, R = H) in a mixture of sulfuric and acetic acid has been examined by Linstead, *et al.*[5] After saponification, the crude *cis-syn*-β-decalol (I, R = H) was isolated in 12.5% yield. (A 25% yield of this decalol was obtained from the precursor of the diene, Δ^3-butenylcyclohexanol, with added acetic anhydride to assist dehydration.) Similarly the homologous diene, produced by dehydration of the tertiary alcohol *in situ*, afforded the *cis*-substance I (R = CH_3)[6] as the only bicyclic product that was identified. Now it is possible that in both of these cases the *cis*-decalin derivative did represent the major cyclization product; however, it was not demonstrated that the total reaction product did not contain significant amounts, or even possibly a preponderance, of the *trans* isomers. Therefore we have repeated the work of Linstead with butenylcyclohexene and, by taking advantage of vapor phase chromatographic techniques, have made a quantitative analysis of the product which in a typical experiment was found to have the following composition (compounds are given in the order of elution); about 16% of starting material, 13% of a cyclic ether (see below), 1–2% of two additional products neither of which was *trans*-Δ^2-octalin, 1.0% of Δ^3-butenylcyclohexanol, 1.8% of an unidentified unsaturated alcohol, 2.8% of an unidentified saturated alcohol which was not identical with any of the β-decalols, and 4.4% of *cis-syn*-2-decalol. The yield of *trans*-2-decalols was less than 0.3%. The remainder of the total reaction product evidently was water soluble (perhaps consisting of glycols or sulfate esters). The major products were separated by preparative vapor phase chromatography and identified with authentic materials by infrared spectroscopic comparison. The ether (see above) is tentatively assigned the structure 2-methyl-5,5-pentamethylenetetrahydrofuran on the basis of the following evidence: (1) the compositional analysis was compatible with the formula $C_{10}H_{18}O$; (2) the infrared spectrum failed to show absorption in the hydroxyl, carbonyl, or olefinic bond region; (3) the n.m.r. spectrum exhibited absorption for one (and only one) proton as a multiplet in the region indicative of the grouping ROCH; (4) the structure is a rational product of hydration, followed by ring closure involving the alcoholic oxygen as the nucleophile.

The possibility that the observation of the formation of a high ratio of *cis*- to *trans*-decalol was due to selective reaction of *trans-syn*-2-decalol (the more likely epimer of *trans* cyclization) to form water-soluble products was disproved by submitting a mixture of *cis-syn*-2-decalol and *trans-syn*-2-decalol to the cycli-

(1) (a) Paper 11 of this series: W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *J. Am. Chem. Soc.*, **86**, 1959 (1964); (b) a preliminary account of the work described in the present paper was reported at the I.U.P.A.C. Meeting in London, July 17, 1963; see W. S. Johnson, *Pure Appl. Chem.*, **7**, 317 (1963).

(2) G. Stork and A. W. Burgstahler, *J. Am. Chem. Soc.*, **77**, 5068 (1955).

(3) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955); see also L. Ruzicka in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 290–310.

(4) Nonclassical carbonium ion intermediates (see ref. 3) would serve as well to preserve the stereochemical integrity of the process, and this alternative possibility is recognized in using the term "synchronous."

(5) R. P. Linstead, A. B. L. Wang, J. H. Williams, and K. D. Errington, *J. Chem. Soc.*, 1136 (1937).

(6) R. P. Linstead, A. F. Millidge, and A. L. Walpole, *ibid.*, 1140 (1937).