Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.79; H, 8.51; N, 20.04.

2,2,7,7-Tetramethylcyclohepta-3,5-dienone (15). A 2.16-g (0.02 mol) sample of 2,5-cycloheptadienone was dissolved in 50 ml of dry *t*-butyl alcohol containing 9.0 g (0.08 mol) of potassium *t*-butoxide. To the ice-cooled solution there was added 14.2 g (0.10 mol) of methyl iodide during 30 min. A work-up similar to that described above gave 2.3 g (70%) of **15**, bp 48–51° (1.5 mm). An analytical sample of **15** was obtained by preparative scale vpc (10% SE-30 on Chromosorb G, 150°); $\nu_{\max}^{\mathrm{CCl_4}}$ 1700, 1660, and 1615 cm^{-1}; $\lambda_{\max}^{\mathrm{isooctane}}$ 235 (5170) and 282 mμ (ϵ 730); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 243 (4680) and 290 mμ (ϵ 710); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ A_2B_2 pattern centered at 5.77 ($J_{AB} = J_{A'B'} = 10$ Hz; $J_{AA'} = 2.8$ Hz; $J_{BB'} = 1$ Hz; 4 H, vinyl protons) and singlet at 1.27 (12 H, methyl groups).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.00; H, 9.83.

Irradiation of 15 on a Preparative Scale. A solution of 1.0 g of **15** in 450 ml of acetone was irradiated as above through Corex optics. After 55 min, the reaction was virtually complete. The solvent was evaporated and the nonpolymeric residue (0.7 g) was subjected to preparative scale vpc. The lone photoproduct was obtained as a colorless oil; $\nu_{\max}^{\mathrm{neat}}$ 1700 cm^{-1}; the nmr spectrum (in $CDCl_3$) displayed singlets at δ 8.73, 8.85, 8.89, and 8.99 (3 H each, methyl groups), a multiplet at 8.26 (2 H, cyclopropyl protons), and a multiplet at *ca.* 4.38 (2 H, vinyl protons). The identity of these spectra with the infrared and nmr spectra of an authentic sample of 3-methyl-4-caren-2-one (**16**)[35] was clearly indicated.

Photolysis Runs. Results of the irradiation of **2** and **15** under a variety of conditions are tabulated in Tables I–III. All of these photolyses were performed in quartz test tubes held in a vertical position on the outer surface of the water-cooled quartz immersion well. In a typical experiment, 250 mg of **15** and 100 mg of cyclooctane (internal standard) were diluted to a specific volume with the solvent of choice (each solvent was purified by appropriate methods until it was homogeneous to vpc). The quartz test tubes were carefully flushed with nitrogen and tightly stoppered with serum caps which permitted withdrawal of aliquots with a microsyringe. An aliquot was removed at time zero and analyzed by vpc.[36] The gas chromatographic unit was carefully calibrated by the procedure utilized in one of our earlier papers.[3] The areas of the various gas chromatographic peaks were determined by cutting and weighing Xerox reproductions of the vpc curves (good quality paper).

In the attempted quenching studies, piperylene (Aldrich) was freshly fractionated prior to use. Naphthalene (reagent grade) was employed as received.

In the sensitized runs, acetone (analytical reagent) and benzophenone (reagent grade) were employed as received.

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[35] We wish to thank Professor Whitham for making available to us the various spectra of authentic **16**.

[36] A 0.125 in. × 10 ft stainless steel column packed with 5% SE-30 on 60–80 mesh Chromsorb W at 155° was employed in conjunction with an Aerograph Hi-Fy Model 600D gas chromatograph equipped with a flame ionization detector.

The Interception of Homoallylic Cations by Neighboring Hydroxyl

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received March 18, 1968*

Abstract: The silver ion induced cyclization of selected *cis*- and *trans*-iodohydrins in which the iodine substituent occupies a homoallylic position has been investigated. Evidence is presented which supports the fact that ring closure proceeds by way of intermediate homoallylic cations which are subject to intramolecular nucleophilic attack by the neighboring hydroxyl group. The ambient electrophilic nature of homoallylic cations is considered in light of the demonstrated selectivity for HO-*n* participation exclusively at only one of the two available sites. In the cases studied, the capability for cyclization is seen to be independent of the geometry of the double bond in the iodohydrin precursor in certain examples, but totally dependent on geometry in other instances. Explanation of these experimental findings in terms of the steric demand imposed by the particular transition state, in turn controlled by relative rates of cyclization, is presented.

Of the various effects which can be exerted by a substituent on the reactions of an organic molecule, that which involves direct or partial bonding of the substituent to the developing or completely unfolded reaction site continues to attract widespread interest.[1] The propensity of such groups as amino,[2] thioether,[3] carboxyl,[4] and alkoxyl[5] for neighboring group participation in certain simple systems has been recognized for some years. In contrast, the neighboring hydroxyl group as such has been little studied,[6] although alkoxide ions produced from such alcohols in alkaline solution have received considerable attention.[1] The great majority of the cases examined have been acyclic and cyclic compounds where the substituent had but one reactive site with which to interact intramolecularly. It was our intent in this work to investigate systems in which a hydroxyl substituent could avail itself of two widely differing sites in the course of intramolecular cyclization. Such a study forms part of our continuing program designed to examine new aspects of oxygen[7] and sulfur[8] neighboring group effects.

[1] B. Capon, *Quart. Rev.* (London), 18, 45 (1964).

[2] (a) H. Freundlich and K. Kroepelin, *Z. Physik. Chem.*, 122, 39 (1926); (b) G. Salomon, *Helv. Chim. Acta*, 16, 1361 (1933).

[3] (a) G. M. Bennett, F. Heathcoat, and A. N. Mosses, *J. Chem. Soc.*, 2567 (1929); (b) G. M. Bennett and E. G. Turner, *ibid.*, 813 (1938); (c) see also W. E. Truce, W. W. Bannister, and R. H. Knopse, *J. Org. Chem.*, 27, 2821 (1962).

[4] J. F. Lane, and H. W. Heine, *J. Am. Chem. Soc.*, 73, 1348 (1951); H. W. Heine, E. Becker, and J. F. Lane, *ibid.*, 75, 4514 (1953).

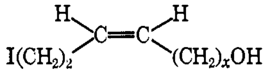
[5] (a) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 3, 1 (1958); (b) E. L. Allred and S. Winstein, *J. Am. Chem. Soc.*, 89, 3991, 3998, 4008, 4012 (1967); (c) E. R. Novak and D. S. Tarbell, *ibid.*, 89, 73, 3086 (1967).

[6] H. W. Heine, A. D. Miller, W. H. Barton, and R. W. Greiner, *ibid.*, 75, 4778 (1953).

[7] (a) L. A. Paquette, *Tetrahedron Letters*, 1291 (1965); (b) L. A. Paquette and H. Stucki, *J. Org. Chem.*, 31, 1232 (1966); (c) L. A. Paquette and R. W. Begland, *J. Am. Chem. Soc.*, 87, 3784 (1965); (d) R. W. Begland and P. C. Storm, unpublished observations in this laboratory.

[8] (a) L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, 89, 6659 (1967); (b) L. D. Wise, results as yet unpublished.

The investigation of such systems was deemed of special interest because of the possible relevance of the results to several important theoretical points among which may be cited the development of our knowledge concerning the phenomenon of neighboring group participation and the factors which control ring closure. For reasons of synthetic accessibility, *cis*- and *trans*-iodohydrins of types **1** and **2** were utilized as substrates. Reaction of **1** and **2** with sources of monovalent silver and characterization of the products which result in the individual cases have been accomplished and the results are here presented and discussed.



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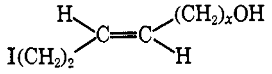

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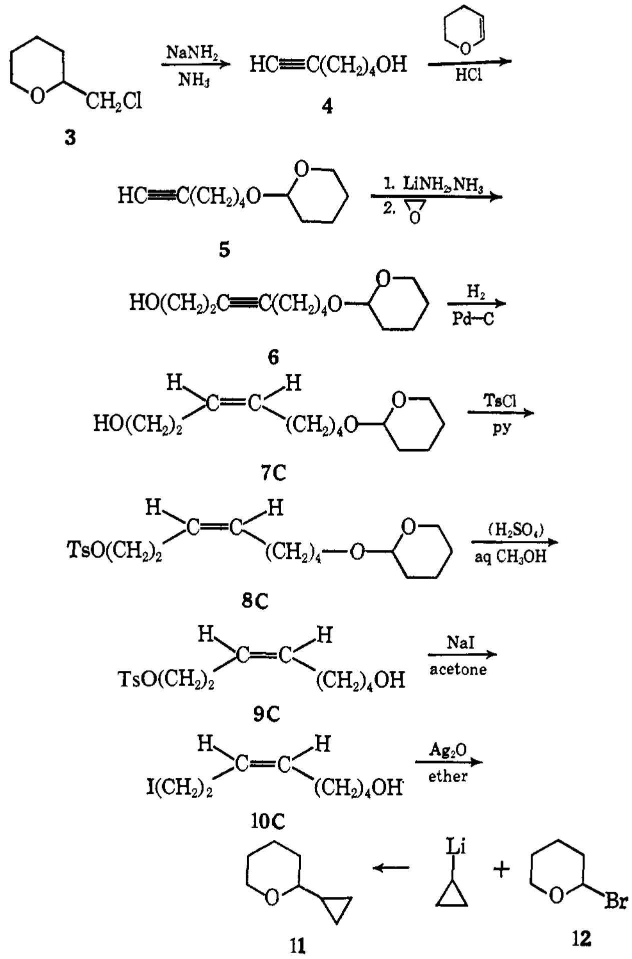
Results

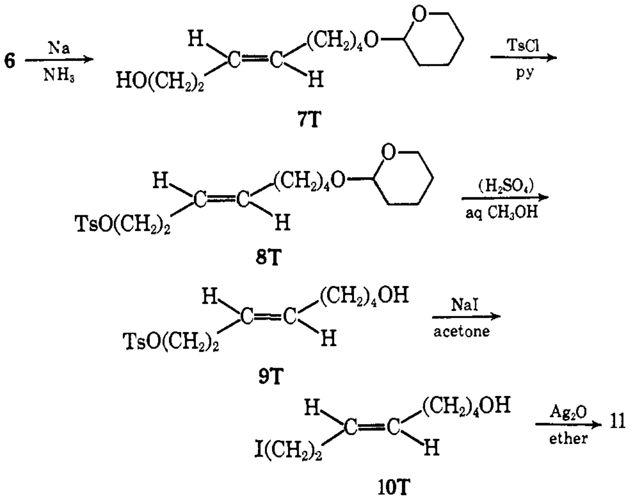
The δ-Hydroxyl Substituent. The synthesis of the isomeric *cis*- and *trans*-8-iodo-5-octen-1-ols (**10C** and **10T**) began in both instances with the conversion of tetrahydropyran-2-methyl chloride (**3**) to 5-hexyn-1-ol (**4**) with sodium amide in liquid ammonia solution (Scheme I). Blocking of the hydroxyl group by treatment of **4** with dihydropyran led to the formation of **5**. Careful addition of excess ethylene oxide to the anion of **5**, prepared *in situ* by means of lithium amide in liquid ammonia, afforded **6** in good yield. Partial catalytic hydrogenation of **6** gave the desired *cis*-olefin **7C** which was subsequently converted into its *p*-toluenesulfonate ester (**8C**) in 83% yield. Removal of the tetrahydropyranyl group resulted in formation of *cis*-hydroxytosylate (**9C**). Without purification, **9C** was transformed into the corresponding iodohydrin **10C** by treatment with sodium iodide in acetone. Slow addition of an ethereal solution of **10C** to a rapidly stirred suspension of powdered silver oxide in ether at room temperature resulted in quantitative formation of silver iodide. Careful work-up of the organic solution led to the isolation of 2-cyclopropyltetrahydropyran (**11**), bp 76–77° (55 mm), in 26% yield and >98% purity, together with somewhat lesser quantities of a mixture of three higher boiling components, bp 105–125° (3.5–0.6 mm), which were not further characterized. The structure of **11** followed from its spectral parameters (see Experimental Section) and was confirmed by independent synthesis from cyclopropyllithium and 2-bromotetrahydropyran (**12**).

Scheme I



The synthesis of **10T**, summarized in Scheme II, was achieved in a series of four steps starting from **6**. The assignment of *trans* stereochemistry to the olefinic linkage introduced during the sodium–liquid ammonia reduction of the triple bond is consistent with the well-recognized stereoselectivity consistently observed in such transformations.[9] When **10T** was gradually added to silver oxide in ether in the predescribed manner, **11** was again isolated (39% yield, >98% purity). Exhaustive distillation likewise afforded an approximately equal amount of significantly higher boiling materials which were not examined.

Scheme II



The γ-Hydroxyl Substituent. 4-Pentyn-1-ol was converted into its tetrahydropyranyl ether and hydroxyethylated using ethylene oxide and lithium amide in liquid ammonia to give **13**. By procedures similar to those employed with **6**, this alcohol (**13**) was transformed into the isomeric *cis*- and *trans*-7-iodo-4-hepten-1-ols, **17C** and **17T**, respectively (see Scheme III). When **17C** was added under conditions of moderately high dilution to a rapidly stirred slurry of powered silver oxide in ether, 2-cyclopropyltetrahydrofuran (**18**) was produced in 47% yield. This volatile liquid gave a single peak when subjected to gas chromatography on several columns, thus establishing that this material was

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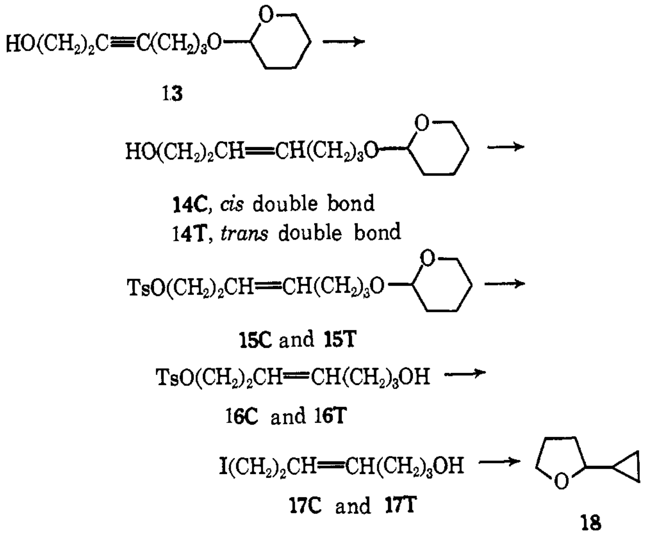
(9) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 71–72.

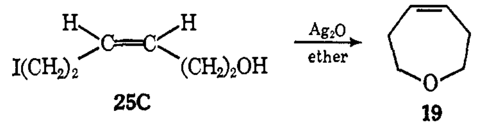
Scheme III



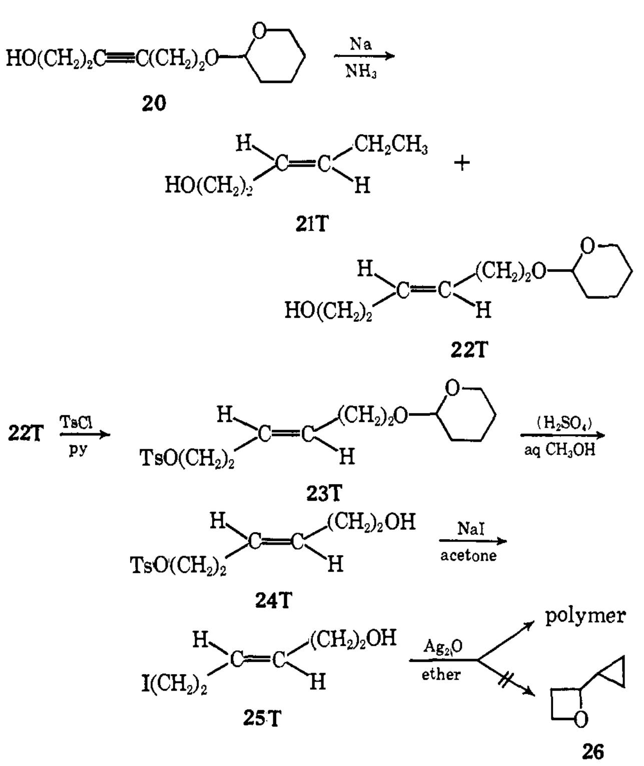
the sole cyclization product. The formulation of **18** as 2-cyclopropyltetrahydrofuran was supported by its elemental analysis and by the great similarity of its infrared and nmr spectra with those of **11**. In particular, the nmr spectrum of **18** (in $CDCl_3$) displayed a five-proton multiplet in the δ 0.1–1.1 region (cyclopropyl ring), a four-proton multiplet at 1.5–2.1 (five-ring methylene groups), and a three-proton multiplet at 3.1–3.8 (>CHO–).

When *trans* iodohydrin **17T** was subjected to similar silver oxide treatment, **18** was again isolated (57% yield) after careful work-up. As in the previous example, **18** was found by vpc to be uncontaminated with other low-boiling products.

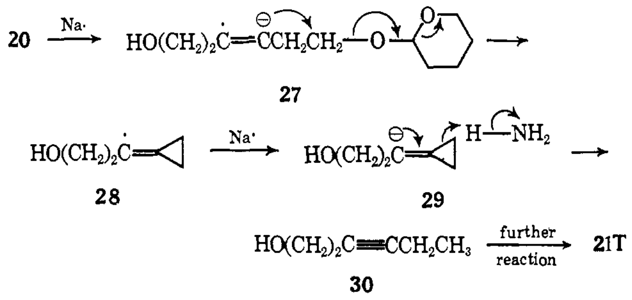
The β-Hydroxyl Substituent. The reaction of *cis*-6-iodo-3-hexen-1-ol (**25C**) with silver oxide in ether has been studied previously by Meinwald and Nozaki[10] who found that 2,3,6,7-tetrahydrooxepin (**19**) was produced in 25% yield and a high state of purity. As in the above examples, quantities of high-boiling materials (apparently a three-component mixture) were formed along with **19**.[10]



Scheme IV



At the outset of the synthesis of *trans* isomer **25T**, sodium in liquid ammonia reduction of acetylenic alcohol **20** was observed to yield two products, the major component of which (34.9%) proved to be the known *trans*-3-hexen-1-ol (**21T**). The alcohol formed in lesser quantities (24.8%) was shown to be the desired *trans*-olefin **22T** (see Scheme IV). The unprecedented production of **21T** can best be rationalized in terms of displacement of the tetrahydropyranyl group from intermediate radical anion **27**. Thus, one-electron reduction of the acetylenic bond in **20** gives rise to radical anion **27**[9] which clearly can cyclize with concomitant 1,3 displacement of the oxygenated function. Rapid reduction of the resulting methylenecyclopropane radical **28** results in conversion to anion **29** which can be expected to rearrange with rupture of the three-membered ring and generation of acetylenic alcohol **30**. Reduction of **30** to **21T** needs no additional mechanistic clarification. Although nucleophilic displacement of tetrahydropyranyloxy groups has not been observed frequently, it is well recognized that 1,3-intramolecular displacements are especially facile;[11] further, intramolecular alkylation reactions of intermediate radical anions derived from carbonyl,[12] α,β-unsaturated carbonyl,[13] and acetylenic functions[14] have recently been shown to be especially useful synthetic reactions.



trans alcohol **22T** was converted to *trans* iodohydrin **25T** according to the established procedure. When an ethereal solution of **25T** was added slowly to a rapidly stirred slurry of powdered silver oxide in anhydrous ether at room temperature, only polymer formation was observed. No low-boiling products could be detected.

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(10) J. Meinwald and H. Nozaki, *J. Am. Chem. Soc.*, **80**, 3132 (1958).

(11) (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 243–256; (b) A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 3914 (1967).

(12) H. O. House, J.-J. Riehl, and C. G. Pitt, *J. Org. Chem.*, **16**, 650 (1965).

(13) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Am. Chem. Soc.*, **87**, 275 (1965).

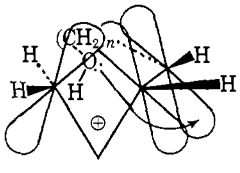
(14) G. Stork, S. Malhotra, H. Thompson, and M. Uchibayashi, *ibid.*, **87**, 1148 (1965).

Discussion

It is now well established that a π bond disposed in β,γ fashion to a developing carbonium ion significantly enhances the rate of ionization, dramatically affects product stereochemistry in rigid systems, and frequently promotes the formation of rearrangement products.[15] The magnititude of this effect has been found to vary substantially as a function of solvent (enhanced in less nucleophilic media) and substitution about the double bond.[16,17] These phenomena have been ascribed to significant delocalization of the neighboring π electron pair, such an interaction leading to the generation of a stabilized cation termed a homoallylic cation.[18] Conceptually, the homoallylic cation may be considered to result from overlap of the vacant p orbital with the most proximate π lobe of the olefinic linkage and to constitute an ambident electrophile, irrespective of whether it is termed a "classical" or "nonclassical" entity.[19] In fact, the capability of a homoallylic cation to offer two alternative sites to an approaching nucleophilic species was first discovered in the early work within the cholesteryl–*i*-cholesteryl series.[20]

The various cyclic ethers produced upon treatment of homoallylic iodides **10C**, **10T**, **17C**, **17T**, and **25C** with silver oxide may arise from two distinctly different mechanistic routes. The first of these pathways involves attack by electrophilic silver ion at the site of the iodine substituent to produce a homoallylic cation which reacts intramolecularly with the neighboring hydroxyl group to give product. Alternatively, it is possible that the hydroxyl group first releases its acidic proton to the somewhat alkaline silver oxide reagent and that cyclization actually results from intramolecular nucleophilic displacement of iodide by neighboring alkoxide ion. To resolve this question iodohydrins **17C** and **17T** were subjected in one instance to the action of aqueous silver nitrate at room temperature, and, in a second set of experiments, to aqueous sodium hydroxide (1 equiv) under identical conditions. Whereas mild treatment with silver nitrate led again to the isolation of 2-cyclopropyltetrahydrofuran (**18**) in yields roughly comparable to those previously obtained, the experiments in alkaline solution were found to give 60–70% recovery of the iodohydrins together with smaller quantities of the related diols. The presence of **18** could not be detected in the latter experiments. These results clearly establish the fact that the cyclizations in question proceed by way of attack of the hydroxyl substituents upon intermediate homoallylic cations.

An analysis of the above data in terms of the structural factors which affect HO-4, -5, -6, and -7[21] involvement and which control the ultimate site of bonding of the hydroxyl group to the electron-deficient homoallylic moiety is now in order. Firstly, the interception of homoallylic cations by neighboring hydroxyl groups is obviously not dependent upon the geometry of the double bond of the iodohydrin precursor if intramolecular nucleophilic attack is to occur at the more highly substituted internal carbon atom of the homoallylic cation (compare **10C** and **10T**, **17C** and **17T**). The steric situation present in the pair of geometric isomers is illustrated in structures **31** and **32**. It is quite evident in these formulas that the carbon center which is to be the ultimate seat of nucleophilic attack is equidistant from the neighboring hydroxyl group in both examples.



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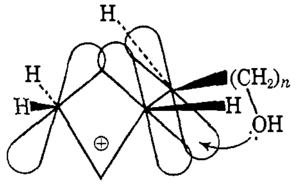

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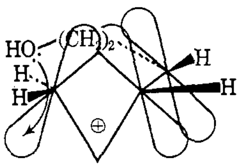
In contrast, a total dependence on geometry obtains in those cases where attack at the less highly substituted terminus of the homoallylic cation is demanded by the structure (compare **25C** and **25T**). The reason for this is quite apparent in structures **33** and **34**. Thus, whereas the hydroxyl group of the *cis* isomer **33** is ideally oriented for approach to the upper lobe of the electron-deficient C-6 carbon atom, the same group in **34** finds itself in a very unfavorable orientation for participation. The important point established by this comparison is that a very large difference in reactivity cannot be reliably predicted for a given *cis–trans* isomer pair unless allowance is made for the fact that intramolecular neighboring group cyclization involving homoallylic cations can take place at two sites which differ considerably in their relationship to the functionalized side chain.



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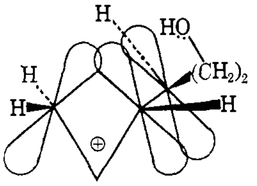

34

It is clearly seen from the foregoing account that the formation of five- (**18**) and six-membered (**11**) oxygen-containing rings is favored and that no detectable quantities of eight- and nine-membered cycles, respectively, were produced. The larger rings could theoretically arise from intramolecular nucleophilic attack at the alternate terminus of the homoallylic cation (HO-8 and HO-9 participation). It is also significant that seven-ring formation (*i.e.*, **19**) is observed, but that the oxetane derivative **26** was not obtained. This behavior is not unexpected and, in fact, finds a great deal in common with the known anchimeric assistance capabilities of neighboring methoxyl,[5] amino,[2] sulfide,[3] and carboxylate groups.[4] A particularly interesting aspect of

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(15) For recent reviews of this subject, see (a) M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967); (b) L. N. Ferguson and J C Nnadi, *J. Chem. Educ.*, **52**, 529 (1965); (c) R. Breslow, in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 4; (d) J. A. Berson, ref 15c, Chapter 3.

(16) (a) M. Hanack, S. Kang, J. Häffner, and K. Görler, *Ann.*, **690**, 98 (1965).

(17) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1331 (1965).

(18) (a) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); (b) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959).

(19) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(20) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946); S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948); S. Winstein and A. H. Schlesinger, *ibid.*, **70**, 3528 (1948).

(21) The symbolism HO-*n* is herein employed to denote the size of the heterocyclic ring (*n* members) ultimately produced (or at least considered producible *a priori*) in the cyclization, as suggested earlier for neighboring methoxyl participation.[5a]

the present study is found in the observations that the neighboring hydroxyl groups in each instance participate by interaction exclusively with only one of the two possible sites on the homoallylic cation.

Experimental Section[22]

5-Hexyn-1-ol (4). This alcohol was prepared by the method of Englington, Jones, and Whiting. From 110 g (0.82 mol) of tetrahydropyran-2-methyl chloride (**3**)[23] and sodium amide (prepared from 56.5 g of sodium metal) in 1500 ml of liquid ammonia, there was obtained 53 g (66%) of **4**, bp 79–80° (13 mm), n^{23}D 1.4490 [lit.[23] bp 75° (16 mm), n^{16}D 1.4510].

6-(2-Tetrahydropyranyloxy)-1-hexyne (5). A well-stirred mixture of 53 g (0.54 mol) of **4** and 44 g (0.54 mol) of dihydropyran was cooled to −30° and treated dropwise with 1 ml of concentrated hydrochloric acid. When the exothermic reaction had subsided, the reaction mixture was treated with a small quantity of powdered potassium carbonate and distilled directly. There was obtained 92 g (93.5%) of **5**, bp 77–78° (0.55 mm), n^{22}D 1.4588, which was used without further purification.

8-(2-Tetrahydropyranyloxy)-3-octyn-1-ol (6). To a stirred mixture of lithium amide (from 3.40 g of lithium wire and ferric nitrate catalyst) in 1000 ml of liquid ammonia was added dropwise during 30 min a solution of 69 g (0.38 mol) of **5** in 100 ml of ether. Stirring was continued for 30 min followed by addition of 50 g (1.13 mol) of ethylene oxide. The resulting solution was stirred for 5 hr, the ammonia was allowed to evaporate, 1000 ml of ether was added, and 75 ml of saturated ammonium chloride solution together with 300 ml of water were slowly added in order. The combined organic layers were dried, the ether was evaporated, and the residue was distilled to give 67 g (78%) of **6**, bp 115–117° (0.04 mm), n^{23}D 1.4820.

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.38; H, 9.75.

***cis*-8-(2-Tetrahydropyranyloxy)-3-octen-1-ol (7C).** A solution of 33.6 g (0.15 mol) of **6** in 150 ml of ethyl acetate containing 0.5 g of 5% palladium on carbon was hydrogenated in a Brown hydrogenator. After the uptake of 1 mol of hydrogen, the catalyst was separated, the filtrate evaporated, and the residue distilled to give 31.9 g (94.5%) of **7C**, bp 116–117° (0.05 mm), n^{24}D 1.4739.

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.60. Found: C, 68.08; H, 10.66.

***cis*-8-(2-Tetrahydropyranyloxy)-3-octenyl *p*-Toluenesulfonate (8C).** A solution of 28.5 g (0.125 mol) of **7C** and 26.8 g (0.14 mol) of *p*-toluenesulfonyl chloride in 100 ml of pyridine was stored at 0° for 24 hr. Water and ether were added, and the ether layer was washed with iced 10% sulfuric acid, water, and sodium bicarbonate solution. The ether layer was dried, and the ether was evaporated to give 40.0 g (83%) of a clear oil, n^{26}D 1.5050, which was used directly.

***cis*-8-Iodo-5-octen-1-ol (10C).** To a stirred mixture of 40.0 (0.104 mol) of crude **8C**, 150 ml of methanol, and 100 ml of water was added dropwise at 0° 11 ml of concentrated sulfuric acid. Stirring was continued for 18 hr, and the mixture was neutralized with solid sodium carbonate. Water was added to dissolve the solid, methanol was removed under reduced pressure, and the residue was extracted with methylene chloride. The organic layer was washed with sodium bicarbonate solution, dried, filtered, and evaporated to give 30.4 g (98%) of **9C**.

The crude **9C** thus prepared (29.0 g, 0.097 mol) and 29.2 g (0.195 mol) of sodium iodide in 600 ml of anhydrous acetone was stirred at room temperature for 1 hr and at reflux for 18 hr. The precipitated solid was filtered, the solvent was evaporated, water and methylene chloride were added, and the organic layer was washed with sodium thiosulfate solution and water, dried, and evaporated. Distillation of the residue gave 21.1 g (86%) of **10C**, bp 112° (0.09 mm), n^{22}D 1.5345.

Anal. Calcd for $C_8H_{15}IO$: C, 37.81; H, 5.95. Found: C, 37.27; H, 5.82.

Cyclization of 10C. A solution of 18.6 g (0.073 mol) of **10C** in 20 ml of anhydrous ether was added dropwise over 4 hr to a rapidly stirred mixture of 35 g (0.15 mol) of freshly prepared silver oxide in 400 ml of anhydrous ether. The resulting slurry was stirred for 5 hr and filtered to remove the salts. The filtrate was carefully distilled to give 2.40 g (26%) of 2-cyclopropyltetrahydropyran (**11**), bp 76–77° (55 mm), n^{21}D 1.4525; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 0.1–1.1 (multiplet, 5 H, cyclopropyl protons), 1.2–2.0 (multiplet, 6 H, ring methylene protons), and 2.35–4.1 (three multiplets, 1 H each, >C*H*O–).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.87; H, 11.20.

More exhaustive distillation afforded 1.72 g of a mixture of three higher boiling products, bp 105–125° (3.5–0.6 mm).

***trans*-8-(2-Tetrahydropyranyloxy)-3-octen-1-ol (7T).** To a solution of 9.2 g (0.40 g-atom) of sodium in 1000 ml of liquid ammonia was added dropwise over 30 min a solution of 30.0 g (0.13 mol) of **6** in 50 ml of ether. The solution was stirred for 2 hr, 600 ml of ether was added, and solid ammonium chloride was added in portions until the blue color no longer persisted. Water was added, and the ammonia was allowed to evaporate. The organic layer was separated, washed with water, dried, and distilled to give 26.3 g (87.4%) of **7T**, bp 116° (0.05 mm), n^{24}D 1.4753.

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.60. Found: C, 68.92; H, 10.47.

***trans*-8-Iodo-5-octen-1-ol (10T).** A 24.5-g (0.11 mol) sample of **7T** was treated as above with 23.0 g (0.12 mol) of *p*-toluenesulfonyl chloride in 100 ml of pyridine. The usual work-up afforded 34.5 g (87%) of **8T**, n^{26}D 1.5080, which was used without further purification. Removal of the dihydropyran blocking group gave 26.0 g (96%) of **9T**, n^{25}D 1.5143.

From 24.5 g (0.082 mol) of **9T** and 24.8 g (0.165 mol) of sodium iodide in 600 ml of anhydrous acetone, there was obtained 18.4 g (88%) of **10T**, bp 110–111° (0.10 mm), n^{22}D 1.5369.

Anal. Calcd for $C_8H_{15}IO$: C, 37.81; H, 5.95. Found: C, 37.77; H, 5.93.

Cyclization of 10T. Dropwise addition of a solution of 13.5 g (0.053 mol) of **10T** in 200 ml of anhydrous ether to a rapidly stirred mixture of 28 g (0.12 mol) of silver oxide in 400 ml of ether over a 4-hr period and subsequent stirring for 5 hr gave 2.63 g (39%) of **11**, bp 82° (57 mm), n^{21}D 1.4530. Infrared and nmr spectra and vpc retention times were identical with those of authentic **11**.

2-Cyclopropyltetrahydropyran (11). To a solution of cyclopropyllithium in 75 ml of ether [prepared from 6.0 g (0.049 mol) of cyclopropyl bromide and 0.76 g (0.11 g-atom) of lithium wire according to the procedure of Seyferth and Cohen[24]] was added dropwise during 30 min a solution of 2-bromotetrahydropyran (**12**) [prepared from 4.30 g (0.051 mol) of dihydropyran according to Paul[25]] in 50 ml of the same solvent. The mixture was stirred at room temperature for 5 hr and filtered to remove the inorganic salts. The filtrate was washed with water, dried, and carefully evaporated. Distillation of the residue afforded 2.10 g (33.8%) of **11** (>95% purity). The nmr and infrared spectra, as well as the vpc retention times on a variety of columns, of a purified quantity, n^{25}D 1.4524, were identical with those of the previous samples.

7-(2-Tetrahydropyranyloxy)-3-heptyn-1-ol (13). Treatment of a mixture of 116 g (1.38 mol) of 4-pentyn-1-ol[26] and 116 g (1.38 mol) of dihydropyran with 1 ml of concentrated hydrochloric acid at −30° afforded 206 g (88.5%) of 5-(2-tetrahydropyranyloxy)-1-pentyne, bp 73–75° (1.7 mm), n^{30}D 1.4532, which was used without further purification.

Condensation of the lithium salt of this acetylene with ethylene oxide in liquid ammonia solution provided **13** in 77% yield, bp 112–114° (0.04 mm), n^{30}D 1.4791.

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.69; H, 9.35.

***cis*-7-(2-Tetrahydropyranyloxy)-3-hepten-1-ol (14C).** Partial hydrogenation of 123 g (0.58 mol) of **13** yielded 117 g (94%) of **14C**, bp 108–110° (0.03 mm), n^{24}D 1.4741.

Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.46; H, 10.60.

***cis*-7-Iodo-4-hepten-1-ol (17C).** From 25.0 g (0.116 mol) of **14C** and 24.8 g (0.13 mol) of *p*-toluenesulfonyl chloride in 75 ml of pyridine, there was obtained 36.5 g (85%) of **15C** as a clear oil, n^{24}D

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[22] The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. The preparative scale gas chromatographic separations were performed with a Varian Aerograph Autoprep Model A-700 unit equipped with thermal conductivity detectors.

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1.5062. Treatment of this oil with sulfuric acid in aqueous methanol gave 27.0 g (96%) of **16C** as a viscous oil which was subjected directly to sodium iodide in acetone solution. Distillation of this reaction product gave 18.6 g (84%) of yellow liquid, bp 97–99° (0.13 mm), n^{28}D 1.5399.

Anal. Calcd for $C_8H_{13}IO$: C, 35.02; H, 5.46. Found: C, 34.95; H, 5.54.

Cyclization of 17C. Dropwise addition of a solution of 29.3 g (0.15 mol) of **17C** in 500 ml of anhydrous ether to a rapidly stirred mixture of 75 g (0.32 mol) of silver oxide in 750 ml of the same solvent gave upon careful work-up 6.56 g (47%) of 2-cyclopropyltetrahydrofuran (**18**), bp 71–72° (70 mm), n^{25}D 1.4430; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.1–1.0 (broad multiplet, 5 H, cyclopropyl protons), 1.5–2.1 (multiplet, 4 H, ring methylene protons), and 3.1–3.8 (multiplet, 3 H, >C*H*O–).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.66; H, 10.77.

***trans*-7-(2-Tetrahydropyranyloxy)-3-hepten-1-ol (14T).** Sodium (13.8 g, 0.6 g-atom) in liquid ammonia (700 ml) reduction of **13** (42.5 g, 0.2 mol) gave rise to 37.4 g (87%) of **14T**, bp 105–106° (0.06 mm), n^{26}D 1.4723.

Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.05; H, 10.38.

***trans*-7-Iodo-4-hepten-1-ol (17T).** From 20.0 g (0.09 mol) of **14T** and 19.1 g (0.10 mol) of *p*-toluenesulfonyl chloride in 60 ml of pyridine, there was obtained 23.1 g (67%) of **15T** as a clear oil, n^{26}D 1.4995. Partial hydrolysis of this oil with sulfuric acid in aqueous methanol gave 16.1 g (90.6%) of **16T**, n^{26}D 1.5091, which was treated directly with sodium iodide in acetone solution to afford 9.5 g (75%) of **17T** as a yellow liquid, bp 88–89° (0.05 mm), n^{25}D 1.5381.

Anal. Calcd for $C_7H_{13}IO$: C, 35.02; H, 5.46. Found: C, 35.08; H, 5.50.

Cyclization of 17T. A 7.1-g (0.030 mol) sample of **17T** was treated with powdered silver oxide (13.9 g, 0.06 mol) in the usual manner. Careful distillation of the reaction product led to the isolation of 1.90 g (57%) of **18**, bp 69–70° (65 mm), n^{24}D 1.4430, identical in all respects with the material obtained from **17C**.

***trans*-6-(2-Tetrahydropyranyloxy)-3-hexen-1-ol (22T).** To a solution of 24.2 g (1.05 g-atom) of sodium in 1500 ml of liquid ammonia was added dropwise a solution of 70 g (0.35 mol) of **20**[10,27] in 100 ml of ether. The resulting solution turned pink and an additional 14 g (0.61 g-atom) of sodium was added. The blue solution was worked up as described above to give 12.3 g (35%) of *trans*-3-hexen-1-ol (**21T**), bp 48–49° (2.4 mm), n^{23}D 1.4390, *p*-nitrophenyl urethan mp 84.0–84.5° [lit.[28] bp 51–53° (9 mm), n^{20}D 1.4374; *p*-nitrophenyl urethan mp 84–85°], and 17.5 g (25%) of **22T**, bp 102–103° (0.08 mm), n^{23}D 1.4748.

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.79; H, 10.09.

***trans*-6-Iodo-3-hexen-1-ol (25T).** From 15.5 g (0.077 mol) of **22T** and 16.3 g (0.085 mol) of *p*-toluenesulfonyl chloride in 80 ml of pyridine, there was obtained 22.5 g (82%) of **23T** as a clear oil. Selective hydrolysis of this oil gave 16.0 g (94%) of **24T** which was converted directly to **25T** in the usual manner, 6.5 g (49%), bp 94–95° (0.05 mm), n^{23}D 1.5418.

Attempted Cyclization of 25T. Reaction of 5.3 g (0.023 mol) of **25T** with 12.7 g (0.055 mol) of powdered silver oxide in the customary fashion produced only a viscous, high-boiling liquid.

Cyclization of 17C with Aqueous Silver Nitrate. A solution of 3.0 g (12.5 mol) of **17C** in 25 ml of tetrahydrofuran was added dropwise during 30 min to a stirred solution of 2.53 g (15 mmol) of silver nitrate in 40 ml of water. A yellow precipitate of silver iodide formed rapidly. The mixture was stirred overnight, filtered, and treated with 100 ml of water. The filtrate was extracted with ether, and the combined organic layers were dried and carefully evaporated. Distillation of the residue gave 0.43 g (31%) of **18**, bp 60–61° (45 mm).

Cyclization of 17T with Aqueous Silver Nitrate. Treatment of 5.0 g (0.021 mol) of **17T** with 4.2 g (0.025 mol) of silver nitrate in the manner described above gave 0.68 (29%) of **18**, bp 66–67° (50 mm).

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Kinetics and Mechanism of Oxidative Coupling of *p*-Phenylenediamines

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Abstract: Coupling reactions between quinonediimine, T^+, and coupler anions such as phenolates, C^-, have been analyzed within the framework of the scheme

$$T^+ + C^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} I \xrightarrow{k_3} P$$

where the second step may be elimination or oxidation. Values for k_1, k_2, and k_3, obtained for several systems, were found to be independent of pH. Coupling was examined from two points of view: (a) the reaction of nucleophiles, *i.e.*, C^-, with T^+ and (b) the reaction of electrophiles, *i.e.*, T^+, with C^-. In experiments related to a, the rates were found to increase with the basicity of C^-. In experiments related to b, reaction of two different couplers with various diimines produced similar rate effects. The reaction of diimines with bulky substituents *ortho* to the primary imino nitrogen deviated from a linear free energy relationship.

The oxidative coupling between *p*-phenylenediamine and a phenolic coupler is a three-component reaction if we consider the oxidant. It is known that the coupling reaction goes through the diimine;[1] however, it is expedient to use a mixture of oxidant and diamine[1c] instead of diimine because of the latter's instability. The oxidation step can be regarded as incidental to the

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