Aryl Norbornane Derivatives. II. The Unusual Preparation of a Carbonate during Performic Acid Oxidation[1]

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RECEIVED JANUARY 9, 1961

2-Phenylnorbornene (I, R = C_6H_5) reacted with excess performic acid to give 2-endo-phenyl-2,3-cis-exo-norbornylene carbonate (IX, R = C_6H_5). The formation of carbonates by the performic acid oxidation of olefins is found not to be a general reaction, but is favored in molecules giving intermediates with eclipsed C–O bonds on adjacent carbon atoms. Similar oxidation of 1-phenylcyclohexene did not give carbonate but did yield cis-diol, providing a further example of this stereochemically abnormal reaction course. Pinacol rearrangement of 2-phenylnorbornane-2,3-cis-exo-diol (VI, R = C_6H_5), the saponification product of the carbonate, gave 3-endo-phenyl-2-norbornanone (XVII). Mechanistic possibilities for these reactions are suggested.

The propensity of bicyclo[2.2.1]heptane derivatives toward rearrangement is well illustrated by the action of performic acid upon olefins in this series. Esters obtained from norbornene (I, R = H) and performic or peracetic acid gave 2,7-diol V (R = H) after saponification.[3,4] Epoxide II (R = H), the probable reaction intermediate, gave the same product with formic acid.[4] Participation of the electrons of the C_1–C_6 bond concomitant with opening of the protonated oxirane ring III (R = H), produced non-classical bridged ion IV (R = H). Exclusive reaction of formic acid at C-1, according to this suggested mechanism, led to rearranged product V (R = H).[3,4] Recently Krieger[5] demonstrated the reaction to be more complicated than originally supposed, but confirmed the absence of both 2,3-cis-exo-diol VI (R = H) and 2,3-trans-diol VII (R = H) in the product. Nucleophilic attack at position C-2 in both III and IV is excluded, even though there are precedents for such processes in other additions to norbornene and its derivatives.[6]

Diols similar in structure to V were obtained from analogous reactions with 9-oxa-endo-trimethylene-2-norbornene,[7] endo-dicyclopentadiene[8] and 3′,-6′-diacetoxybenzonorbornadiene.[9] Only when functional groups are present which can participate in epoxide ring openings are non-rearranged products formed.[10]

Peracid glycolations of olefins generally give trans-1,2-diols.[11] We have been intrigued by the

possibility of obtaining cis-1,2-diols from suitably substituted norbornenes or their epoxides as a consequence of steric or electronic factors. However, exo-trimethylene-2-norbornene,[6] 1-methylnorbornene[12] and 2-methylnorbornene[12] (I, R = CH_3) gave rearranged products. Vicinal diols were shown to be absent by quantitative periodic acid determinations.[6,12] Continuation of this quest with 2-phenylnorbornene (I, R = C_6H_5) as the olefin and performic acid as the oxidant resulted in the unusual outcome reported in the present paper.

Experimental Results

Proof of Structure of the Oxidation Product.—Diol monoformates, the initial products from the action of performic acid upon olefins,[11,13] are commonly not characterized but are saponified to the desired glycols immediately.[3–11] A white crystal-

(1) Paper VII of a series on Bridged Ring Systems; paper VI, D. C. Kleinfelter and P. von R. Schleyer, J. Org. Chem., in press (1961). Taken in part from the Ph.D. Thesis of D.C.K., Princeton University, 1960.

(2) Procter and Gamble Fellow, 1958–1959. National Science Foundation Summer Fellow, 1959. We are indebted to the National Science Foundation for a grant which supported a large part of this work in 1959–1960.

(3) H. Kwart and W. G. Vosburgh, J. Am. Chem. Soc., 76, 5400 (1954); H. Kwart and G. C. Gatos, ibid., 80, 881 (1958).

(4) H. M. Walborsky and D. F. Loncrini, ibid., 76, 5396 (1954); J. Org. Chem., 22, 1117 (1957).

(5) (a) H. Krieger, Suomen Kemi., B31, 340 (1958), and refs. therein cited; cf. also (b) S. B. Soloway and S. J. Cristol, J. Org. Chem., 25, 327 (1960).

(6) For a summary see L. Kaplan, H. Kwart and P. Schleyer, J. Am. Chem. Soc., 82, 2341 (1960).
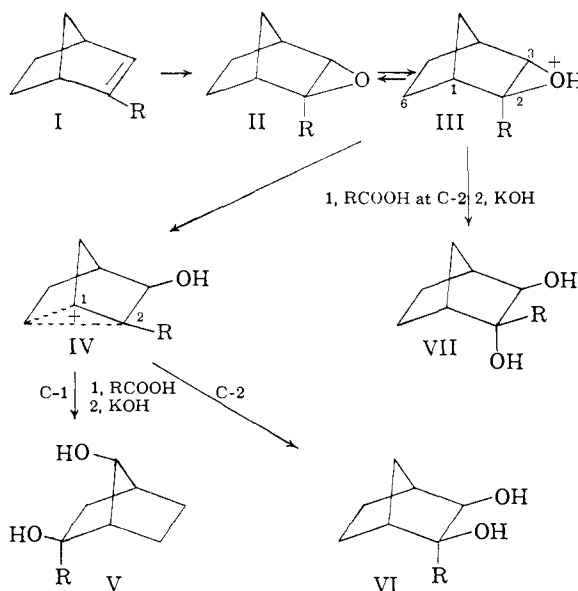
(7) E. L. Eliel and C. Pillar, ibid., 77, 3600 (1955).

(8) M. Gates and S. P. Malchick, ibid., 76, 1378 (1954); K. Alder, F. H. Flock and H. Wirtz, Ber., 91, 609 (1958).

(9) J. Meinwald, H. Nozaki and G. A. Wiley, J. Am. Chem. Soc., 79, 5579 (1957); J. Meinwald and G. A. Wiley, ibid., 80, 3667 (1958).

(10) (a) J. A. Berson and S. Suzuki, ibid., 80, 4341 (1958); (b) H. B. Henbest and B. Nicholls, J. Chem. Soc., 221 (1959).

(11) (a) D. Swern, Chem. Revs., 45, 1 (1949), Org. Reactions, 7, 378 (1953); (b) S. Winstein and R. B. Henderson in R. C. Elderfield, Ed.,

"Heterocyclic Compounds," Vol. 1, J. Wiley and Sons, Inc., New York, N. Y., 1950, Chapt. 1, p. 1; (c) R. E. Parker and N. S. Isaacs, Chem. Revs., 59, 737 (1959); (d) F. D. Gunstone in R. A. Raphael, E. C. Taylor and H. Wynberg, Eds., "Advances in Organic Chemistry," Vol. 1, Interscience Publ., Inc., New York, N. Y., 1960, p. 103.

(12) Unpublished observations of P. R. S.

(13) (a) D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, J. Am. Chem. Soc., 67, 1786 (1945); (b) W. J. Hickinbottom and D. R. Hogg, J. Chem. Soc., 4200 (1954); (c) A. F. Plate and A. A. Mel'nikov, Zhur. Obshchei Khim., 30, 935 (1960); A. F. Plate, A. A. Mel'nikov, T. A. Stalinskaya and P. A. Zelenko', ibid., 30, 1250 (1960); A. F. Plate, A. A. Mel'nikov and A. A. Ovezova, ibid., 30, 1256 (1960).

line material, isolated in 11% yield, was produced directly from 2-phenylnorbornene (I, R = C_6H_5), a slight excess of 30% hydrogen peroxide and formic acid. A clue to the structure of this substance was the unusual 1820 cm.$^{-1}$ carbonyl band in its infrared spectrum. Functional groups which can absorb at this position are few.[14] A carbonate structure appeared to be most likely for the product, an interpretation supported by the microanalytical results. Saponification gave a diol cleavable by periodic acid,[15] which showed absorptions in the 3 μ region of the infrared ($\Delta\nu$ = 97 cm.$^{-1}$, Table I) characteristic of strong intramolecular OH...O hydrogen bonds[16] but not of interactions of the OH...C_6H_5 type.[17] This evidence is compatible with a *cis*-vicinal structure such as VI (R = C_6H_5) or VIII (R = C_6H_5) but excludes both *trans* (as VII, R = C_6H_5) and rearranged (V, R = C_6H_5) possibilities. 2,7-Diols V are inert to periodic acid.[3-10,12,15] The azimuthal angle between C–O bonds in VII is 120°; hydrogen bonding between the hydroxyl groups would be impossible[16] (Table I).

TABLE I
SPECTRAL SHIFTS IN CYCLIC DIOLS

Compound, diol	$\Delta\nu$, cm.$^{-1}$
Norbornane-2-*exo*-7-*syn*- (V, R = H)	76[3], 62[5]
Norbornane-2,3-*cis*-*exo*- (VI, R = H)	103[3]
Norbornane-2,3-*cis*-*endo*- (VIII, R = H)	102[3]
Bornane-2,3-*cis*-*exo*-	95[a,b]
Bornane-2,3-*cis*-*endo*-	96[a], 90[b]
Bornane-2-*exo*-3-*endo*-	0[a,b]
Bornane-2-*endo*-3-*exo*-	0[a,b]
2-Phenylnorbornane-2,3-*cis*-*exo*- (VI, R = C_6H_5)	97[c]
Cyclopentane-1,2-*cis*-	61[18]
Cyclopentane-1,2-*trans*-	0[18]
Cyclohexane-1,2-*cis*-	39[18]
Cyclohexane-1,2-*trans*-	32[18]
1-Methylcyclohexane-1,2-*cis*-	44[d]
1-Phenylcyclohexane-1,2-*cis*-	29[e], 57[f]
trans-2-Phenylcyclohexanol	23[e,f]

[a] S. J. Angyal and R. J. Young, *J. Am. Chem. Soc.*, **81**, 5467 (1959). [b] T. Takeshita and M. Kitajime, *Bull. Chem. Soc. Japan*, **32**, 985 (1959). [c] 2-OH...O(C-3) bonding. For geometrical reasons, OH...C_6H_5 hydrogen bonding is not possible. There appears to be no enhancement of $\Delta\nu$ due to the inductive effect of the phenyl group. [d] Apparent $\Delta\nu$; A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 4391 (1956). [e] OH...C_6H_5 hydrogen bonding. [f] Apparent $\Delta\gamma$. The free peak is the 2-OH, the bonded peak is due to 1-OH...O(C-2) bonding (see Cole and Jefferies, cited above, for a discussion). The $\Delta\nu$ is enhanced by the greater acidity of the 1-OH because of action of the electron-withdrawing phenyl substituent.

VIII   IX
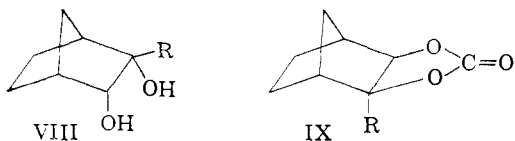
(14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1958.

(15) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Fourth Edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 129.

(16) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).

(17) P. von R. Schleyer, D. S. Trifan and R. Bacskai, *ibid.*, **80**, 6691 (1958); P. von R. Schleyer, C. Wintner, D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. 14, 1 (1959).

There is no known exception to the general rule that additions to the norbornene double bond occur preferentially from the *exo* side provided that no hindering *syn*-7 substituents are present in the molecule.[18] *exo*-Products have been found in epoxidations[3-12] and in *cis*-glycolations with permanganate.[3,7,9,11d,19] Oxidation of 2-phenylnorbornene (I, R = C_6H_5) with potassium permanganate should give 2-*endo*-phenylnorbornane-2,3-*cis*-*exo*-diol (VI, R = C_6H_5); the product of this reaction was identical with the diol from the performic acid route. The carbonate, therefore, has structure IX (R = C_6H_5). Phosgene converted diol VI (R = C_6H_5) to carbonate IX (R = C_6H_5).

Mode of Formation of Carbonate and Isolation of 1-Phenylnortricyclene (XI).—The stoichiometry of the oxidation which led to carbonate required two moles of performic acid. The reaction was repeated using varying amounts of hydrogen peroxide. A large excess of oxidant gave the maximum yield of carbonate, 54–56%. Diol VI (R = C_6H_5) gave a 76% yield of carbonate IX (R = C_6H_5) when treated with performic acid under the same conditions.

The starting material, 2-phenylnorbornene (I, R = C_6H_5), was prepared by KHSO$_4$ dehydration of 2-*exo*-phenyl-2-norbornanol (X).[1] An isomeric by-product, 1-phenylnortricyclene (XI) which might not react with performic acid, should also be present.[1,20] A 21% yield of XI was obtained by work-up of the carbonate mother liquors. This hydrocarbon was identified by bands in its infrared spectrum at 12.65 and 11.9 μ, characteristic of nortricyclenes[21] and of 1-substituted nortricyclenes,[22] respectively. The ultraviolet spectrum of XI (principal band at 226 mμ, log ϵ 4.10) resembled that of phenylcyclopropane (λ_{max} 220 mμ, log ϵ 3.92).[23] Structure XI was also consistent with the n.m.r. spectrum of the hydrocarbon.[24] Mercuric oxide oxidation of the hydrazone of 1-phenyl-2-norbornanone (XII)[1]—the standard nortricyclene synthesis[25]—gave rise to the same compound.

X OH   XI   XII
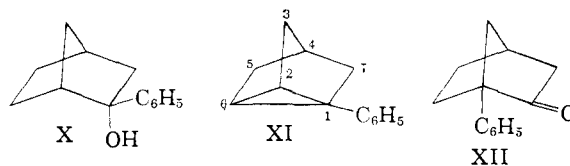
(18) K. Alder, G. Stein and H. F. Rickert, *Ann.*, **525**, 221 (1936); K. Alder and W. Roth, *Ber.*, **87**, 161 (1954), and numerous other examples.

(19) K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 2822 (1957).

(20) P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

(21) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(22) P. von R. Schleyer and R. E. O'Connor, Abstracts, 134th National Meeting, Am. Chem. Soc., Chicago, Ill., Sept., 1958, p. 39P; H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959).

(23) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947).

(24) We are indebted to Dr. George van Dyke Tiers for the determination and interpretation of the n.m.r. spectra.

(25) E. Josephy and F. Radt, Eds., "Elsevier's Encyclopaedia of Organic Chemistry," Vol. 13, Elsevier Publ. Co., Inc., New York, N. Y., 1940; K. Alder, *et al.*, *Ann.*, **593**, 23 (1955); E. J. Corey, S. W. Chow and R. A. Scherrer, *J. Am. Chem. Soc.*, **79**, 5773 (1957).

The maximum yield of carbonate rises to 65–67% when the calculation is adjusted for the presence of inert 1-phenylnortricyclene (XI) in the starting material. Most of the rest of starting olefin I (R = C_6H_5) was converted to acids of unestablished structure. Phenol was present in this acid fraction. These acid products probably arose by cleavage to ketoacid XIII, for which reaction many precedents are available,[13c,26] followed by Baeyer–Villiger oxidation and hydrolysis during work-up. No appreciable amount of hydroxyformate was present. By-products in the runs employing less of an excess of performic acid were not investigated, however.

XIII　　　　　　　　XIV C_6H_5
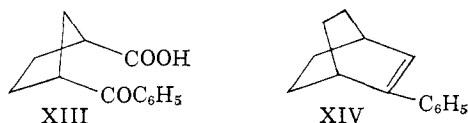
The Scope of the Carbonate Reaction.—We have not been able to find recorded in the literature a single additional example of carbonate formation from performic acid oxidation of olefins.[26a] In most instances the intermediates, assumed to be hydroxyformates, were hydrolyzed to the desired diols without characterization. Carbonates may have been present in some cases but were undetected. We have examined the reaction products of a few olefins to see whether carbonates were formed in other instances.

2-p-Chlorophenylnorbornene (I, R = p-ClC_6H_4) gave a 55% yield of solid carbonate IX (R = p-ClC_6H_4). The crude reaction product from performic acid and 2-phenylbicyclo[2.2.2]octene (XIV) showed carbonate as well as formate bands in the infrared spectrum. No carbonate bands were present in the spectra of crude products from oxidation of either 1-phenylcyclopentene[13c,26] or 1-phenylcyclohexene.

The diol from the latter olefin was examined in greater detail because of apparently conflicting prior reports. The older literature stated that aqueous acid hydrolysis of 1-phenylcyclohexene oxide gave equal amounts of cis (m.p. 96°) and trans (m.p. 99°) 1-phenylcyclohexane-1,2-diols.[27] A recent paper claimed that trans-diol (m.p. 96°) was produced in 80% yield from the reaction of 1-phenylcyclohexene with monoperphthalic acid.[28] The diol (m.p. 95°) from performic acid oxidation of the same olefin appeared to be homogeneous and to be identical with the diol of Filler, Camara and Naqvi.[28] The configuration was shown to be cis rather than trans by direct comparison with 1-phenylcyclohexane-1,2-cis-diol prepared by osmium tetroxide oxidation[1d,27] (see Table I). The formation of cis-diols from phenyl-substituted epoxides

may now be considered to be a general reaction[11c]; further discussion is presented in the sequel.

The Pinacol Rearrangement of 2-Phenylnorbornane-2,3-cis-exo-diol (VI, R = C_6H_5).—Vicinal diols in the norbornane series do not normally undergo the pinacol rearrangement with facility. Norbornane-2,3-cis-exo-diol (VI, R = H) was very resistant to the action of acids; under forcing conditions tars and a 20% yield of 2-norbornanone were formed.[29] Tertiary vicinal diols derived from bicyclic terpenes do react with mineral acids, but the products appear to be monocyclic rather than those expected from normal pinacol rearrangements.[30] The phenyl group of diol VI (R = C_6H_5) should facilitate reaction with strong acids and should tend to prevent the cleavage reaction.[30]

With dilute aqueous sulfuric acid–dioxane and short reaction times, diol VI (R = C_6H_5) gave a ketone not identical with 3-exo-phenyl-2-norbornanone (XV).[31] This latter compound had been prepared from the Diels–Alder adduct of β-nitrostyrene and cyclopentadiene (XVI),[32] now known to have the exo-phenyl, endo-nitro configuration,[33] by reduction of the double bond followed by the Nef reaction.[31] The stereochemistry of XV—phenyl group exo—is rather firmly established by this sequence.

2,4-DNP,
m.p. 166°[31]
XV

NO₂
XVI

2,4-DNP,
m.p. 204°
XVII
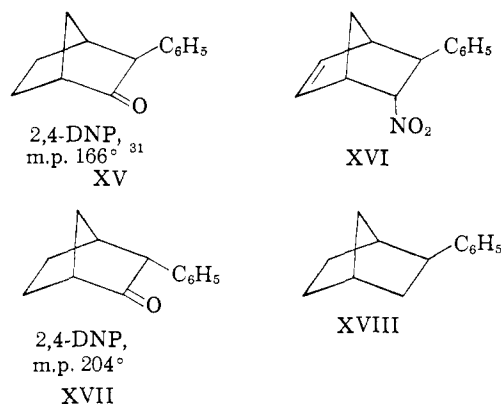
XVIII

Wolff–Kishner reduction of the ketone from the pinacol rearrangement gave 2-exo-phenylnorbornane (XVIII), identical with the benzene–norbornene alkylation product.[1,34] The structure of XVIII was confirmed by n.m.r. spectroscopy.[24] Both the rearrangement ketone and the Nef ketone (XV) *lack* an "adjacent methylene" (–CO–CH_2–) absorption band[35] in the 1400–1440 cm.$^{-1}$ region

(26) J. P. Vila and R. Crespo, *Anales real. soc. españ., fis. y quim.*, **48B**, 273 (1952); *C. A.*, **47**, 3802 (1953).

(26a) For carbonate formation during chromic acid oxidation, see: W. A. Mosher, F. W. Steffren and P. T. Lansbury, *J. Org. Chem.*, **26**, 670 (1961).

(27) J. Boëseken, *Ber.*, **56**, 2409 (1923); *Rec. trav. chim.*, **47**, 683 (1928); C. J. Mann, *ibid.*, **48**, 332 (1929); P. E. Verkade, J. Coops, Jr., C. J. Mann and A. Verkade, *Ann.*, **467**, 217 (1928).

(28) R. Filler, B. R. Camara and S. M. Naqvi, *J. Am. Chem. Soc.*, **81**, 658 (1959); *cf.* R. E. Lyle and G. C. Lyle, *J. Org. Chem.*, **18**, 1058 (1953); S. Nametkin and N. Iwanoff, *Ber.*, **56**, 1805 (1923).

(29) J. G. Traynham, *Chemistry & Industry*, 1142 (1958). Professor H. Kwart (personal communication) also has noted the similar inertness of various norbornane-2,3-diols.

(30) The literature has been summarized and product structures and mechanisms have been suggested by P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1956, pp. 297–298.

(31) W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).

(32) C. F. H. Allen, A. Bell and J. W. Gates, Jr., *ibid.*, **8**, 373 (1943).

(33) J. Weinstock, M. C. Flores and M. Schwarz, Abstracts, Third Delaware Valley Regional Meeting, Am. Chem. Soc., Philadelphia, Penna., Feb., 1959, p. 46.

(34) L. Schmerling, U. S. Patent 2,480,267, Aug. 30, 1949 (*C. A.*, **44**, 1136 (1950)).

(35) S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951); R. N. Jones and A. R. H. Cole, *J. Am. Chem. Soc.*, **74**, 5648 (1952); R. N. Jones, A. R. H. Cole and B. Nolin, *ibid.*, **74**, 5662 (1952); B. Nolin and R. N. Jones, *ibid.*, **75**, 5626 (1953); A. R. H. Cole and D. W. Thornton,

of their infrared spectra. The precise position of this methylene scissoring vibration depends upon ring size and molecular environment; some 20 norbornanone derivatives and a number of cyclopentanones which we have examined all absorbed from 1400 to 1410 cm.$^{-1}$ provided that a methylene group adjacent to the carbonyl function was unsubstituted.[36] 2-Norbornanones substituted upon C-3, such as fenchone and camphenilone, lack this band.

On the basis of this evidence, both the rearrangement ketone and the Nef ketone must be 3-phenyl-2-norbornanone stereoisomers. The Nef ketone is XV; the rearrangement ketone must be XVII, with the phenyl group *endo*.

When the pinacol rearrangement was carried out under more vigorous conditions, or when ketone XVII was heated in basic media, epimerization to XV resulted. *exo*-Substituents are known to be more stable in this series.[37] Epimerization also took place during the course of the Wolff–Kishner reduction of XVII to XVIII.

Discussion

The Formation of Carbonate.—The literature records several instances of *cis*-diol formation from epoxide ring openings.[11c,27] This steric course was observed with styrene and stilbene derivatives[27,38] and with phenyl-substituted cyclic epoxides such as 2α,3α-epoxy-3β-phenylcholestane[39] and the compounds studied in the present work. Of the mechanisms which have been proposed to account for this stereochemistry, the double inversion process involving phenyl participation appears to be the most likely.[11c,40] Phenyl participation during ring opening of protonated 2-phenylnorbornane epoxide III (R = C$_6$H$_5$) would give intermediate XIX and product XX. An alternative pathway involving carbon instead of phenyl participation would proceed from III (R = C$_6$H$_5$) to IV (R = C$_6$H$_5$) to XXI.

Had the reaction been arrested at the monoester stage, or had the epoxide opening been carried out with a carboxylic acid which would not give carbonate, the determination of the structure of the hydroxy ester would have provided mechanistic information. Under the conditions employed here, both XX and XXI might equilibrate with "hemi-ortho ester" XXII. Oxidation to carbonate IX by performic acid might occur

J. Chem. Soc., 1007 (1956); T. Burer and H. H. Gunthard, *Helv. Chim. Acta*, **40**, 2054 (1957); and A. R. H. Cole and R. L. S. Willix, *J. Chem. Soc.*, 1212 (1959). The last reference cites literature reviews; for others see R. N. Jones and C. Sandorfy in W. West, Ed., "Chemical Applications of Spectroscopy," Interscience Publ., Inc., New York, N. Y., 1956, pp. 498–501; L. J. Bellamy, cited in ref. 14, p. 23.

(36) *Cf.* E. J. Corey, M. Ohno, S. W. Chow and R. A. Scherrer, *J. Am. Chem. Soc.*, **81**, 6305 (1959); H. Krieger, *Suomen Kemi.*, **B31**, 112 (1958); **B34**, 24 (1961).

(37) For references see P. von R. Schleyer and M. M. Donaldson, *ibid.*, **82**, 4645 (1960).

(38) See ref. 11c for a summary; also J. Boëseken, *Rec. trav. chim.*, **47**, 683 (1928).

(39) R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 24 (1957).

(40) The experimental observation that the same compound—presumably secondary monoacetate, tertiary alcohol—was formed by the action of peracetic acid on 1-phenylcyclohexene and by esterification of 1-phenylcyclohexane-1,2-*cis*-diol (Lvle and Lyle, ref. 28) is easily explained by the double inversion mechanism; also *cf.*, J. Brewster, *J. Am. Chem. Soc.*, **78**, 4061 (1956).
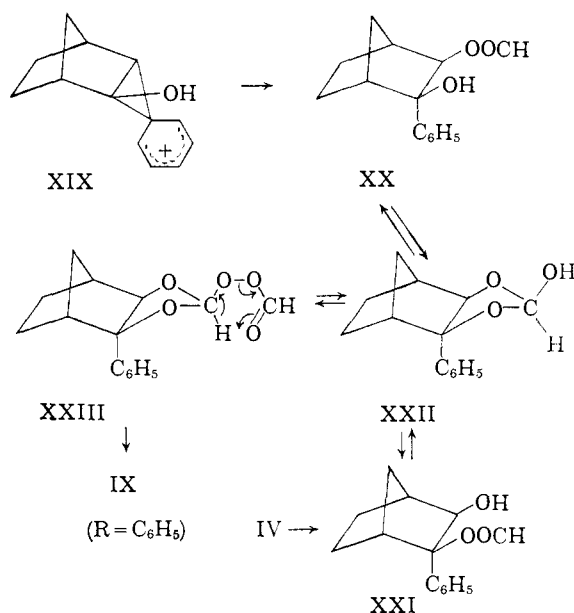
intermolecularly or through ortho perester XXIII. The coplanarity of the two C–O bonds of the rigid norbornane molecule should favor cyclization. Our experimental observations on the oxidation of several olefins suggest that low values of the azimuthal angle between adjacent C–O bonds are required for carbonate formation.[41] The transformation of diol VI (R = C$_6$H$_5$) to carbonate IX (R = C$_6$H$_5$) by the action of performic acid evidently proceeds *via* XX by initial esterification.

The Pinacol Rearrangement.—The simplest mechanism for the pinacol rearrangement—formation of benzyl carbonium ion from the diol, and then a shift of the *endo*-hydrogen from C-3 to C-2—is excluded by the stereochemistry of the product XVII.

Loss of the C-3 hydrogen as a proton from the benzylic carbonium ion would give enol XXIV. Kinetically controlled ketonization should favor protonic attack from the less hindered *exo* side of the molecule[13] and lead to *endo*-phenyl ketone XVII.[42] The possibility of both the hydride shift and the enolization mechanisms for rearrangements of this type has been demonstrated in simpler systems.[43]

There is considerable experimental evidence that migrations from the 3- to 2-position of the norbornane system occur specifically with *exo* substituents.[44] This is consistent with the stereochemical requirements of the bridged ion intermediates.[44]

(41) Both 1,3-dioxolane (W. Shand, quoted by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950)) and ethylene carbonate (C. J. Brown, *ibid.*, **7**, 92 (1954)) have non-planar structures, but the deviations from planarity are not as great as that in cyclopentane (K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959); F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, *ibid.*, **81**, 4915 (1959)); see Table I and ref. 16.

(42) H. E. Zimmerman and T. W. Cutshall, *ibid.*, **81**, 4305 (1959), and previous papers in the same series.

(43) J. B. Ley and C. A. Vernon, *J. Chem. Soc.*, 2987, 3256 (1957). However, for contrary views see W. B. Smith, R. E. Bowman and T. J. Kmet, *J. Am. Chem. Soc.*, **81**, 997 (1959); C. J. Collins, *Quart. Revs. (London)*, **14**, 357 (1960).

(44) Ref. 30, p. 182ff; A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

XXIV   XXV
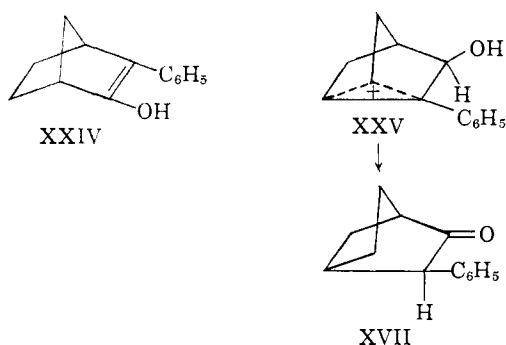
XVII

Were IV (R = C_6H_5) to rearrange to XXV by a 6,1-hydride shift,[44] a suitable precursor of *endo*-3-phenyl-2-norbornanone (XVII) would be formed. The available evidence does not permit a choice between these two mechanistic possibilities.

Experimental

All melting points were taken in soft glass capillaries in a Hershberg apparatus using calibrated Anschütz thermometers. All boiling points are uncorrected. Infrared spectra were taken with Perkin–Elmer model 21 spectrometers; lithium fluoride optics were used in the 3μ region. A Varian instrument was used for the 40 mc. n.m.r. determinations.[24] Microanalyses were carried out by G. Robertson, Florham Park, N. J.

2-*endo*-Phenyl-2,3-*cis-exo*-norbornylene Carbonate (IX, R = C_6H_5). A. Initial Experiment.—To a stirred solution of 10 ml. (11.1 g.) of *ca*. 30% hydrogen peroxide (0.10 mole) and 42 ml. of 98–100% formic acid maintained at 10° was added slowly 12.0 g. (0.07 mole) of 2-phenylnorbornene (I, R = C_6H_5).[1] The two layers which formed initially did not change noticeably overnight. The mixture was poured into 200 ml. of water, heavily salted, and extracted three times with ether. The ether extracts were washed once with dilute sodium bicarbonate solution and then dried over anhydrous sodium sulfate. After the ether was removed under reduced pressure, a yellow oil and some solid remained. The mixture was dissolved in hot ethanol; cooling gave 1.8 g. of white crystals (0.0078 mole, 11.2%). The m.p., 101.3–101.6°, was constant after two recrystallizations from ethanol.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.82; H, 6.04.

The reaction was repeated several times at a temperature of 35–45°. With a ratio of 2.4 moles of hydrogen peroxide per mole of olefin, the yield of carbonate isolated was 26%. With the higher ratio of 3.8, the yield was 35%. Finally, with a ratio of 4.5, the yield of carbonate isolated was 47% (see below).

B. Procedure for Maximum Yield.—The reaction was conducted as above at 35–45° with the following quantities of materials: 150 ml. (165 g., 1.45 moles) of 30% hydrogen peroxide, 400 ml. of 98–100% formic acid and 55.0 g. (0.32 mole) of olefin I (R = C_6H_5). A yield of 35.2 g. (0.15 mole, 47%) of solid carbonate IX (R = C_6H_5) was obtained from ethanol. A quantitative infrared analysis of the evaporated filtrate indicated the additional presence of 5.2–6.3 g. of carbonate. This filtrate was dissolved in ether and washed with sodium bicarbonate solution until neutralization was effected. The combined aqueous portions were acidified, and extracted with ether. The dried solvent was evaporated leaving 11.1 g. of a mixture of unidentified acids. A strong odor of phenol was present; in a later run some phenol was isolated by distillation during the work-up.

The neutral oily residue after the sodium bicarbonate extraction and evaporation of solvent was chromatographed through alumina. A hydrocarbon, 12.4 g. (23%), later identified as 1-phenylnortricyclene (XI), was eluted plus an insignificant amount of biphenyl, an impurity which had been present in the starting olefin.[1] The total yield of carbonate was 40.4–41.5 g. (54–56%, which is increased to 65–67% considering the presence of inert XI in the starting material).

1-Phenylnortricyclene (XI).—The 1-phenylnortricyclene from the preceding experiment was distilled, b.p. 121–122.5° (13 mm.), n^{20}D 1.5581. A portion of the middle fraction was analyzed.

Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.54; H, 8.30.

The ultraviolet spectrum in ethanol had maxima at 226, 260, 269 and 276 mμ, log ϵ's 4.10, 2.93, 2.84 and 2.44, respectively. Phenylcyclopropane possesses maxima at 220, 255 (broad) and 274 mμ, log ϵ's 3.92, 2.75 and 2.45, respectively.[23] The infrared spectrum in CS_2 solution had a medium intensity peak at 12.65 μ (nortricyclene[21]) and a strong absorption at 11.9–11.95 μ (1-substituted nortricyclene[22]). The n.m.r. spectrum, CCl_4 solution, Si(CH_3)$_4$ reference,[24] had the following absorptions in τ-units, with the number of protons indicated in parentheses: 2.962 ± 0.003 (5), the phenyl hydrogens[45]; 7.68 (1), the bridgehead hydrogen at C-4 (XI); 8.419 ± 0.004 doublet (2), methylene at C-7; 8.549 ± 0.002 (4), the methylenes at C-3 and at C-5; 8.56 shoulder (2), the C-2 and C-6 hydrogens on the cyclopropane ring.

Synthesis of 1-Phenylnortricyclene (XI).—The procedure employed was patterned after that used by Corey, Chow and Scherrer[25] for the preparation of 8-bromotricyclene. To a solution of 12.0 g. (0.065 mole) of 1-phenyl-2-norbornanone[1] in 36 ml. of ethanol and 4.0 g. of acetic acid was added 12.0 g. (0.37 mole) of 98% hydrazine, and the solution was refluxed for 4 hours. After removal of most of the solvent at reduced pressure, water was added and the solid which crystallized was filtered. The pale yellow solid was washed with water and dried to give 10.8 g. (0.054 mole, 87% yield based on the assumption that this crude material was all hydrazone). Approximately 0.5 g. was recrystallized three times from ethanol; about 30 mg. remained, m.p. 187.0–188.0°.

Anal. Calcd. for $C_{13}H_{16}N_2$ (hydrazone): C, 77.96; H, 8.05. Calcd. for $C_{26}H_{28}H_2$ (azine): C, 84.74; H, 7.66. Found: C, 85.32, H, 7.78.

The recrystallized product evidently was azine. It had no 3500–3300 cm.$^{-1}$ N–H absorption in the infrared. The composition of the crude product was not determined.

To a solution of 10.3 g. (0.052 mole) of crude 1-phenyl-2-norbornylhydrazone in 75 ml. of ethanol was added 22.0 g. (0.10 mole) of freshly prepared mercuric oxide and the mixture was refluxed for 24 hours. The cooled mixture was filtered, the solid was washed with petroleum ether, and the combined solvents were evaporated. The residue was taken up in ether, washed with saturated aqueous sodium chloride, and dried with sodium sulfate. Distillation gave a first cut of 3.7 g., b.p. 122–129° (12 mm.), n^{20}D 1.5581 and a second cut of 0.7 g., b.p. 131–139° (12 mm.), n^{20}D 1.5461. The infrared spectrum of the first cut was identical with that of XI isolated from performic acid oxidation. The second cut was mainly XI, contaminated with 1-phenyl-2-norbornanone (hydrolyzed hydrazone). The total yield of crude 1-phenylnortricyclene was 4.4 g. (0.026 mole, 49%).

2-Phenylnorbornane-2,3-*exo-cis*-diol (VI, R = C_6H_5). A. By Hydrolysis of Carbonate IX (R = C_6H_5).—Saponification of 4.4 g. (0.019 mole) of 2-*endo*-phenyl-2,3-*cis-exo*-norbornylene carbonate (IX, R = C_6H_5) was effected by refluxing with 2.8 g. (0.05 mole) of potassium hydroxide dissolved in 15–20 ml. of water and 125 ml. of ethanol. The work-up was completed by solvent evaporation, the addition of water and salt, extraction with ether several times, drying and evaporating the solvent, and distillation. A yield of 3.4 g. (0.017 mole, 88%) of a viscous milky-white oil, b.p. 195–199° (12–13 mm.), was obtained. The diol solidified upon standing to a gummy white solid, which could not be crystallized from a wide variety of solvents. The periodic acid test for vicinal diols[15] was positive. In very dilute CCl_4 solution, the diol had concentration independent bands at 3621 and 3524 cm.$^{-1}$ in the infrared.

The *p*-nitrobenzilidene derivative of 2-phenylnorbornane-2,3-*exo-cis*-diol was prepared in the usual manner.[4] Two recrystallizations from ethanol gave material of constant m.p., 172.1–172.7°.

(45) Dr. Tiers[24] reports that this position is the highest yet observed for monoalkyl substituted benzene. An electronic rather than a local magnetic effect is suggested.

Anal. Calcd. for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.32; H, 5.76; N, 4.21.

B. Hydroxylation of 2-Phenylnorbornene (I, R = C₆H₅).—The procedure was similar to that of Bartlett and Bavley[46] and of Kwart and Vosburgh.[3] A 250-ml. erlenmeyer flask was charged with 14.4 g. (0.085 mole) of 2-phenylnorbornene, 150 ml. of A. R. acetone and 12.8 g. (0.081 mole) of potassium permanganate. The reaction mixture was stirred mechanically at 0–7° for 0.5 hour. The precipitated manganese dioxide was filtered, the filtrate was treated with sodium bisulfite to reduce excess permanganate, and filtration repeated. The filtrate was concentrated at water-pump pressure on the steam-bath; the residue was extracted with ether and the ether solution washed with saturated aqueous sodium chloride. After drying the ether solution with sodium sulfate, the solvent and then the product were distilled. A forerun of 1.2 g. of 1-phenyl-nortricyclene (XI), b.p. 119–120° (12 mm.), $n^{20}D$ 1.5601, was collected. 2-Phenylnorbornane-2,3-*cis-exo*-diol was obtained as a cloudy light yellow oil, b.p. 194–200° (12–13 mm.), in a yield of 3.25 g. (0.016 mole, 19%). The infrared spectrum was virtually identical with that of the diol from A, above, except for small carbonyl bands at 1751 and 1686 cm.$^{-1}$, probably due to further oxidation of the diol.

The *p*-nitrobenzylidene derivative had m.p. 172.0–173.0°. No mixed melting point depression was observed with the derivative from part A.

Conversion of 2-Phenylnorbornane-2,3-*cis-exo*-diol (VI, R = C₆H₅) to 2-*endo*-Phenyl-2,3-*cis-exo*-norbornylene Carbonate (IX, R = C₆H₅). A. With Phosgene.—A solution of 480 mg. (2.35 mmoles) of 2-phenylnorbornane-2,3-*cis-exo*-diol in 20 ml. of ligroin, 10 ml. of benzene and a few ml. of pyridine was saturated with phosgene for 10 minutes. The solution was poured into water, 25 ml. of ether added, and the solvent evaporated. Crystallization from ethanol of the yellow oil which remained gave 220 mg. (0.96 mmole, 41%) of carbonate. After two recrystallizations from ethanol the m.p. was 101.2–101.8°; there was no mixed m.p. depression.

B. With Performic Acid.—To a solution of 10 ml. of 98–100% formic acid and 4 ml. (4.5 g., 0.040 mole) of 30% hydrogen peroxide was added 2.0 g. (9.8 mmoles) of 2-phenylnorbornane-2,3-*cis-exo*-diol. Stirring was continued for 24 hours and then the solution was poured into water. A white solid separated; filtration gave 1.6 g. (7.0 mmoles, 71% yield) of carbonate, m.p. and mixed m.p. 101.1–101.8°.

2-*p*-Chlorophenyl-2,3-*cis-exo*-norbornylene Carbonate (IX, R = *p*-ClC₆H₄).—From 12.0 g. (0.060 mole) of 2-*p*-chlorophenylnorbornene,[47] 30 ml. (33 g., 0.30 mole) of 30% hydrogen peroxide and 75 ml. of 98–100% formic acid, 8.5 g. (0.032 mole, 54%) of carbonate was obtained, m.p. 111.1–111.8°, after two recrystallizations from ethanol. The carbonyl band was at 1823 cm.$^{-1}$ in the infrared, CCl₄ solution.

Anal. Calcd. for $C_{14}H_{13}O_3Cl$: C, 63.52; H, 4.95; Cl, 13.40. Found: C, 63.58; H, 5.00; Cl, 13.21.

3-*endo*-Phenyl-2-norbornanone (XVII).—A mixture of 15 ml. of dioxane, 25 ml. of 50% (vol.) sulfuric acid and 4.1 g. (0.020 mole) of 2-phenylnorbornane-2,3-*cis-exo*-diol (VI, R = C₆H₅) was heated on a steam-bath for 0.5 hr. and then poured into ice-water. The resultant oil was extracted with ether. The ether extracts were dried and the solvent evaporated. The residue was distilled to give 2.1 g. (0.011 mole, 55% yield) of colorless oil, b.p. 166–174° (15–17 mm.), $n^{20}D$ 1.5552. The ketone absorbed at 1748 cm.$^{-1}$ in the infrared, a characteristic position for 2-norbornanones. The presence of a hydroxyl band indicated that some unreacted diol had distilled with the ketone.

The 2,4-dinitrophenylhydrazone derivative of 3-*endo*-phenyl-2-norbornanone was recrystallized three times from ethanol–ethyl acetate to constant m.p., 203.7–204.1°.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95; N, 15.29. Found: C, 62.09; H, 5.15; N, 15.00.

3-*exo*-Phenyl-2-norbornanone (XV).—The Nef reaction was carried out on 2-*exo*-phenyl-3-*endo*-nitronorbornane as

previously recorded.[31] The ketone product gave a 2,4-dinitrophenylhydrazone derivative which had a wide m.p. range, ca. 167–184°, after four recrystallizations from ethanol; reported[31] m.p. 165–166° dec.

When the pinacol rearrangement of 2-phenylnorbornane-2,3-*cis-exo*-diol (VI, R = C₆H₅) was carried out at reflux temperature for over an hour, the 2,4-DNP of the product had a similar m.p. range of ca. 159–178°, after three recrystallizations from ethanol. A mixed m.p. of the two samples was ca. 165–183°. A similar result was obtained from the ketone isolated after heating 3-*endo*-phenyl-2-norbornanone (XVII) with sodium hydroxide in ethylene glycol solutions. These products may all have been mixtures of *endo* (XVII) and *exo* (XV) ketones.

2-*exo*-Phenylnorbornane (XVIII).—The Huang-Minlon[48] modified Wolff–Kishner reduction of 1.35 g. (7.3 mmoles) of 3-*endo*-phenyl-2-norbornanone (XVII) was carried out in the usual fashion with 1.5 ml. of hydrazine hydrate in 25 ml. of ethylene glycol. Distillation of the product through a micro apparatus gave 0.75 g. (4.4 mmoles, 60% yield) of clear colorless hydrocarbon, b.p. 124–126° (15–16 mm.), $n^{20}D$ 1.5444. Its infrared spectrum was identical with that of a sample of 2-*exo*-phenylnorbornane, b.p. 125–128° (14–15 mm.), $n^{20}D$ 1.5445 (lit.[34] b.p. 102° at 3 mm., $n^{20}D$ 1.5445), prepared in 65% yield by the alkylation of benzene with norbornene.[34]

The n.m.r. spectrum of 2-*exo*-phenylnorbornane[24] in CCl₄ solution showed the following absorptions, in τ-units: 2.894 ± 0.003, phenyl hydrogens; a multiplet centering at 7.29, the benzylic hydrogen; 7.64, the bridgehead hydrogens. The remaining hydrogens gave an indistinct pattern with peaks at 8.21, 8.56, 8.74 and 8.95 τ.

2-Phenylbicyclo[2.2.2]octene (XIV) was prepared in 93% yield from the addition of phenylmagnesium bromide to bicyclo[2.2.2]octanone; the alcohol which formed apparently dehydrated during the distillation; b.p. 138–145° (14–15 mm.). The ultraviolet spectrum in ethanol had λ_{max} 252 mμ, log ε 4.13.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.74; H, 8.47.

From 5.0 g. of this olefin, 13 ml. of 30% hydrogen peroxide and 30 ml. of formic acid there was obtained, after reaction and work-up in same manner as above, 3.85 g. of crude product. This showed infrared carbonyl bands at about 1820 and 1740 cm.$^{-1}$, indicative of carbonate and formate groups. No further characterization of the product mixture was undertaken. Presumably the epoxide intermediate opened with retention of configuration.

1-Phenylcyclohexane-1,2-*cis*-diol from Oxidation of 1-Phenylcyclohexene. A. With Performic Acid.—1-Phenyl-cyclohexene, prepared in 87.8% yield by KHSO₄ dehydration of 1-phenylcyclohexanol, was treated with performic acid in the usual manner. From 23.7 g. (0.15 mole) of olefin, 63 ml. (69.5 g., 0.63 mole) of 30% hydrogen peroxide and 175 ml. of 98–100% formic acid, there was obtained a crude residue after work-up which showed no carbonate band in the infrared. Hence, it was saponified directly. The residue was dissolved in 200 ml. of ethanol and 12.0 g. (0.21 mole) of potassium hydroxide in aqueous solution added, and the solution was refluxed. The product, 1-phenylcyclohexane-1,2-*cis*-diol, was isolated in 19.5 g. yield (0.10 mole, 67%), after one recrystallization from ligroin. Two more recrystallizations gave material of constant m.p., 94.2–95.0° (lit.[25] m.p. 96°).

The monobenzoate derivative of 1-phenylcyclohexane-1,2-*cis*-diol had m.p. 158.8–159.4°. The monobenzoate reported by Filler, Camara and Naqvi[25] had m.p. 159°.

B. Attempted Oxidation with Potassium Permanganate.—The literature reports that the *cis*-diol can be prepared by potassium permanganate oxidation.[27] We could not obtain diol using the method described above.[3,46] Besides recovered starting material, an oil was obtained which showed both hydroxyl and carbonyl absorptions in the infrared.

C. With Osmium Tetroxide.[11d]—The quantities 0.66 g. of 1-phenylcyclohexene, 0.25 g. of osmium tetroxide, 20 ml. of ether and 1 ml. of pyridine were stirred together for 2 hours. The brown osmiate which formed was filtered, washed with ether, and stirred for 12 hours with 2.0 g. of mannitol and 20 ml. of 10% aqueous potassium hydroxide

(46) P. D. Bartlett and A. Bavley, *J. Am. Chem. Soc.*, **60**, 2416 (1938).

(47) From the acetolysis product of 1-*p*-chlorophenyl-2-*endo*-norbornyl tosylate (to be reported in a subsequent paper). An olefin having similar properties was obtained by potassium bisulfate dehydration of 2-*p*-chlorophenyl-2-*endo*-norbornanol.

(48) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946); **70**, 2802 (1948); **71**, 3301 (1949).

solution. Ether was used to extract the resultant mixture. The combined extracts were dried and the solvent evaporated. There remained 150 of diol, m.p. 93.6–94.4°, after two recrystallizations from ligroin. A mixed m.p. with a sample of the diol from the performic acid reaction product was 93.8–94.6°. The infrared spectra of the two samples were superimposable; the high resolution 3 μ hydrogen bonding spectra showed identical positions and intensities of absorption, 3619, 3590 and 3562 cm.$^{-1}$.

Performic Acid Oxidation of 1-Phenylcyclopentene.— Potassium bisulfate dehydration of 1-phenylcyclopentanol

gave 1-phenylcyclopentene, b.p. 109–113° (15 mm.), n^{20}D 1.5732. The compound solidified in an ice-bath and melted at room temperature (lit.[49] m.p. 22–23°). Performic acid oxidation of this olefin was conducted in the usual manner. The infrared spectrum of the crude product was devoid of carbonate bands; hence, the reaction was not pursued further. This olefin is very prone to ketone formation and cleavage under these conditions.[13c,26]

(49) G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 451 (1956).

[Contribution from the Department of Chemistry, the University of San Francisco, San Francisco 17, Calif., Varian Associates, Palo Alto, Calif.]

Synthesis of Two New Quercitol (Deoxyinositol) Stereoisomers. Nuclear Magnetic Resonance and Optical Rotatory Configurational Proofs[1,2]

By G. E. McCasland,[3] Stanley Furuta, L. F. Johnson[4] and J. N. Shoolery[4]

Two new optically active diastereomeric quercitols (cyclohexanepentols), m.p. 258° and 248°, were obtained by addition of hydrogen bromide to (+)-1,2-anhydro-*allo*-inositol, and subsequent hydrogenolysis. Analysis of the nuclear magnetic resonance spectra of the 248° diastereomer and its bromoquercitol precursor, together with chemical evidence, indicated that the 248° diastereomer has the configuration (123/45); the 258° diastereomer then necessarily has the configuration (125/34). Optical rotation calculations by the methods of Whiffen and Brewster permitted assignment of absolute configurations XIII and XV to the 258° and 248° isomers, respectively. Rotatory dispersion measurements gave, as expected, only plain dispersion curves. The configurational assignments finally were confirmed by chemical correlations, based on formation of the 248°, but not the 258°, diastereomer on direct hydrogenation of the diastereomeric (+)-1,2-anhydro-*neo*-inositol.

The generic name *quercitol* has been proposed for the deoxyinositols (cyclohexanepentols). Ten diastereomers, six active and four *meso*, would be predicted for the quercitols (see Table I and Chart I). Six of these ten had been reported when our present work was started.[5] Two (*proto* and *vibo*) were from botanical sources, and four (*scyllo*, *epi*, *neo*, *cis*) had been prepared by synthesis only. Two additional synthetic diastereomers, *gala* and *talo*, are described in the present article. Since completion of the experiments now reported, the last remaining active diastereomer (*allo*),[6,7,7a] and the

(1) Presented at the I.U.P.A.C. Symposium on the Chemistry of Natural Products, in August, 1960, at Sydney, Australia. Taken in part from the M.S. Thesis of Stanley S. Furuta, Graduate School, University of San Francisco, 1961.

(2) Paper XI on cyclitol chemistry by G. E. McCasland and co-workers; for preceding paper see *J. Am. Chem. Soc.*, **79**, 160 (1957).

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(5) For reviews of previous work on the quercitols, see: (a) S. J. Angyal and L. Anderson in Vol. 14, "Advances in Carbohydrate Chemistry," Academic Press, Inc., New York, N. Y., 1959; (b) R. L. Lohmar, Jr., "The Carbohydrates," by W. Pigman (Editor), Academic Press, Inc., New York, N. Y., 1957, pp. 268–296.

(6) We have recently prepared the racemic *allo* diastereomer (m.p. 262°) and its pentaacetate, m.p. 94°; this work will be described in a separate publication.

(7) After completing the synthetic part of our present work, we learned from M. Nakajima (June, 1960) that by reduction of epoxides or bromoquercitols he has prepared the pentaacetates of *rac-gala-*, *talo-* and *allo*-quercitols, and of *meso-muco*-quercitol. He has also made the racemic form of free *talo*-quercitol. Professor Nakajima (by addition of aqueous hydrogen bromide to epoxides) reportedly also has prepared six new *meso* or racemic diastereomers of bromoquercitol, one or two of which may correspond to our optically active bromoquercitols. We are indebted to Professor Nakajima for helpful consultation by correspondence, and in personal discussions at Melbourne, Australia, in August, 1960.

(7a) Note added in proof.—The work of M. Nakajima (with N. Kurihara) has now been published; see *Chem. Ber.*, **94**, 515 (1961).

Table I

The Quercitols or Deoxyinositols

Formula, configuration, prefix	M.p., °C., and spec. rotations Quercitol	Pentaacetate
meso-Diastereomers		
VII, (12345), *cis*	235–240 d.	163
VIII, (1245/3), *muco*[a]	. . . . .	168
V, (135/24), *scyllo*	235	190
VI, (15/234), *neo*	239 d.	182
Active or racemic diastereomers		
XV, (123/45), *talo*	248, +61°	183, +28°
IV, (1234/5), *allo*[a,b]	DL 262	DL 94
III, (1235/4), *epi*	194, −5°	125, . .
	(DL 208)	(DL 143)
II, (124/35), *vibo*	181, −50°	125, −22°
	(DL 163)	(DL 114)
XIII, (125/34), *gala*	258, −48°	117, −24°
I, (134/25), *proto*	237, +26°	. .[c]

[a] M. Nakajima, personal communication, July, 1960. [b] S. Furuta and G. E. McCasland, unpublished work. [c] Pentaacetate was amorphous; pentabenzoate, m.p. 155°.

last remaining *meso* diastereomer (*muco*),[7] have been synthesized.

Methods which have been used for quercitol synthesis[5] include: reduction (hydrogenation) of inososes, inosose oximes or deoxyinososes; hydrogenolysis of bromoquercitols; hydrogenation of a quinonetetrol; and reduction of anhydro-inositols.[7] The reduction of anhydro-inositols (see below) now appears to be the most convenient and general route.

His quercitols were made from bromoquercitols, not directly from epoxides. Nakajima's products included the racemic form (m.p. 190–191° dec., pentaacetate 158–159°) of our active (125/346) bromoquercitol. He also made the racemic form (m.p. 214° dec.) of our active (123/456) bromoquercitol.