Mechanism of the Prins Reaction. Stereoaspects of the Formation of 1,3-Dioxanes

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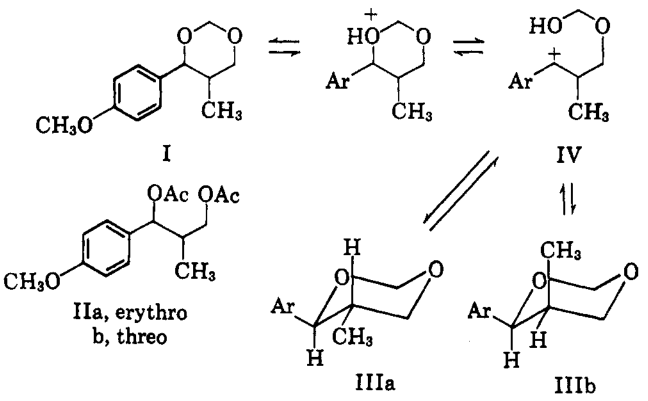
N.m.r. analysis of 1,3-dioxanes formed in the Prins reaction of aromatic olefins indicates a *cis* addition of two formaldehyde units. A possible mechanism is discussed.

The mineral acid catalyzed condensation of formaldehyde with olefins, commonly known as the Prins reaction,[1] is useful for the preparation of 1,3-dioxanes, 1,3-glycols, and their derivatives.[2] It was previously reported that glycol formation proceeds by a *trans*[3,4] diaxial[5] addition of formaldehyde and water and the formation of 1,3-dioxanes proceeds by a *trans* addition of formaldehyde.[4]

Recent work has demonstrated thermodynamic control to be operative[6] in the Prins reaction if the initially formed carbonium ion is highly stabilized. When anethole was refluxed with paraformaldehyde in glacial acetic acid a mixture of 4-anisyl-5-methyl-1,3-dioxane (I) and 1-anisyl-2-methyl-1,3-diacetoxypropane (IIa and IIb) was obtained. The diacetate mixture consisted of 25% IIa and 75% IIb.

Since thermodynamic control operates in diacetate formation, it was anticipated[6] that the *m*-dioxane I could be formed by a similar process and would be a mixture of *cis* and *trans* isomers (IIIa and IIIb) with the equilibrium involving the highly stabilized *p*-methoxybenzyl carbonium ion (IV).



Acid-catalyzed hydrolysis of *m*-dioxane I to 1-anisyl-2-methyl-1,3-propanediol (V)[6] was not attempted because rapid isomerization of the benzylic hydroxylic group would be expected and resulting hydrolysis products could not be unequivocally related to I. This became evident when glycol Va was heated with formic acid and was found to yield a 1:1 mixture of diols Va and Vb. Moreover, if either diol Va or Vb was heated with aqueous formaldehyde (slightly acidic due to formic acid) a *m*-dioxane was obtained which was identical with the product obtained in the acetic acid catalyzed system.[6]

In order to analyze the composition of I an n.m.r. study was performed utilizing 4-anisyl-5-methylpropylene carbonate (VIa and VIb) as a model system. The carbonates were prepared by the reaction of phosgene on diols Va and Vb. The *cis* (VIa) and *trans* (VIb) isomers could be distinguished from each other by the chemical shifts of the 5-methyl and the 4-benzylic protons. The doublet of the C-4 proton due to coupling with the C-5 proton is 3 c.p.s. for VIa and 10 c.p.s. for VIb as shown in Table I. These values are consistent with previously established coupling constants for dihedral angles of 60 and 180°, respectively.[7–9]

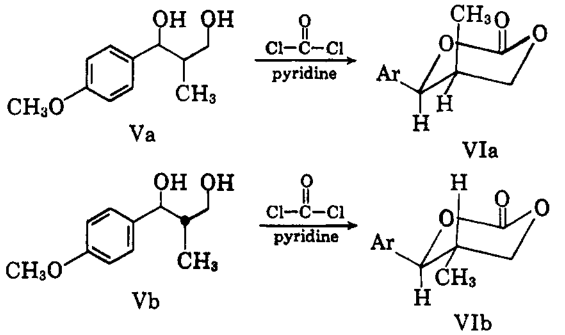


TABLE I

CHEMICAL SHIFTS OF *cis*- AND *trans*-4-ANISYL-5-METHYLPROPYLENE CARBONATE

	δ, p.p.m.	
	4-Benzylic H	5-Methyl H
cis (VIa)	5.55 (J = 3 c.p.s.)	0.85
trans (VIb)	4.98 (J = 10 c.p.s.)	0.82

N.m.r. was selected as the logical tool for analysis of unknown *m*-dioxane I. An n.m.r. spectrum of I indicated the presence of only *one* isomer [verified with gas–liquid chromatography (g.l.c.)]; the coupling constant of the benzylic proton was 10 c.p.s. suggesting a *trans* (IIIa) relationship for the C-4 and C-5 hydrogens.

One isomer is not consistent with thermodynamic control and the configuration (*trans*) of the dioxane I is not in accord with *trans* addition of formaldehyde to a *trans* olefin (anethole). The observed configuration is consistent with *cis* addition of two formaldehyde units.[10]

Further studies were performed utilizing other *trans* aromatic olefins; 4-(3,4-methylenedioxyphenyl)-5-methyl-1,3-dioxane (VII) was prepared by the method of Drukker and Beets[12] from *trans*-isosafrole. Gas–liquid chromatography and n.m.r. spectroscopy indicated one isomer. Coupling of the C-4 proton with the C-5 proton was 10 c.p.s. indicating a *trans* diaxial

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(1) H. J. Prins, *Chem. Weekbald*, **16**, 1510 (1919).

(2) F. Arundale and L. A. Mikeska, *Chem. Rev.*, **51**, 505 (1952).

(3) E. E. Smissman and R. A. Mode, *J. Am. Chem. Soc.*, **79**, 3447 (1957).

(4) A. T. Blomquist and J. Wolinsky, *ibid.*, **79**, 6025 (1957).

(5) E. E. Smissman and D. T. Witiak, *J. Org. Chem.*, **25**, 471 (1960).

(6) P. S. Portoghese and E. E. Smissman, *ibid.*, **27**, 719 (1962).

(7) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

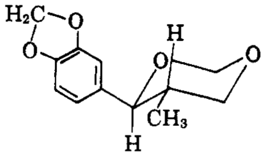
(8) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(9) A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *Tetrahedorn*, **19**, 2145 (1963).

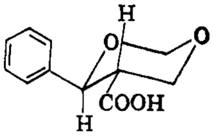
(10) A similar result was recently reported for the β-bromostyrene series.[11]

(11) L. Bernardi and A. Leone, *Tetrahedron Letters*, **10**, 499 (1964).

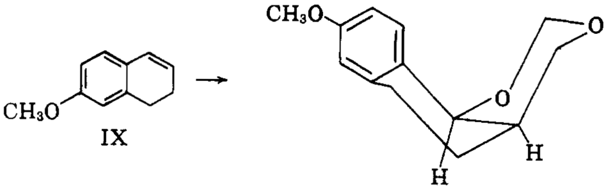
(12) E. A. Drukker and M. G. J. Beets, *Rec. trav. chim.*, **70**, 29 (1951).



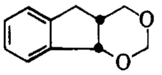
VII



VIII



IX X



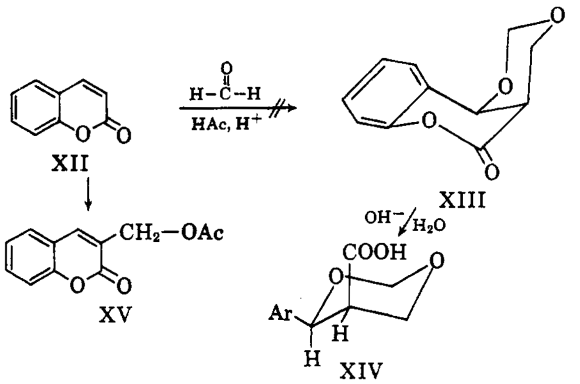
XI

relationship, the product of *cis* formaldehyde addition. The same result was obtained for 4-phenyl-5-carboxy-1,3-dioxane (VIII) prepared from *trans*-cinnamic acid according to the directions of Brugman and Arens.[13] Again the coupling constant of the benzylic proton was 10 c.p.s. These results clearly indicate that in the case of *trans* aromatic olefins, formaldehyde adds by a *cis* process in *m*-dioxane formation.

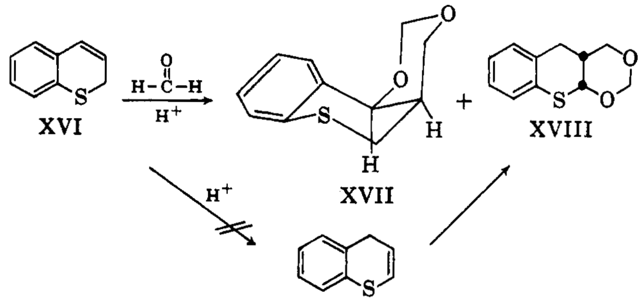
In order to study the generality of the *cis* addition an investigation with *cis* cyclic aromatic olefins was undertaken. When 7-methoxy-1,2-dihydronaphthalene (IX) was treated with formaldehyde under Prins conditions, a low yield of *m*-dioxane X was obtained. In this case the coupling constant of the benzylic proton was 3 c.p.s. suggesting a B,C-*cis* ring juncture; a result expected from *cis* addition of formaldehyde. Indene was transformed to its *m*-dioxane XI by the method of Beets and van Essen[14] and again n.m.r. spectroscopy showed the formation of a *cis*-B,C ring juncture (J_{benz} = 4 c.p.s.).

A low coupling constant may not necessarily indicate a *cis* ring juncture since a distorted *trans* ring juncture would give rise to a dihedral angle of less than 180° for the vicinal protons and thus a lower *J*-value. It was reasoned that the Prins reaction on coumarin (XII) would provide a system with a closed B,C ring juncture (XIII) and, after base-catalyzed lactone hydrolysis, the open nondistorted *m*-dioxane XIV would be available for study. A measurement of the benzylic proton coupling constant before and after hydrolysis would indicate the true nature of the dioxane ring juncture. Coumarin was condensed with paraformaldehyde in the presence of acetic–sulfuric acid solution. The only Prins product obtained was a 75% yield of the unsaturated acetate XV with a yellow tar accounting for the remainder.

As an alternate approach, the Prins reaction utilizing 2H-1-benzothiopyran (XVI)[15] was studied. Reaction with 40% formaldehyde in the presence of sulfuric acid provided a 44% yield of two isomeric *m*-dioxanes XVII and XVIII in about equal amounts. Acid-catalyzed isomerization of XVI to XIX does not account for the formation of *m*-dioxane XVIII since no isomerization

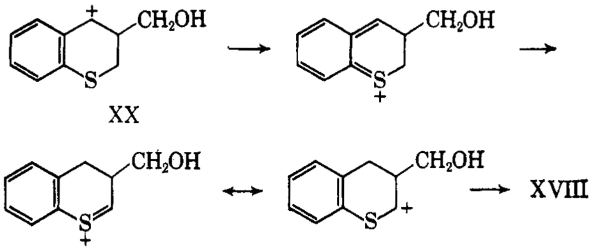


XII XIII XV XIV



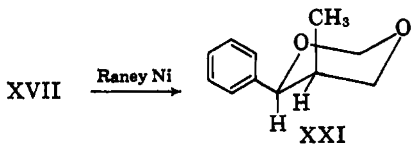
XVI XVII XVIII XIX

occurred when XVI was subjected to reaction conditions without formaldehyde. It is possible that *m*-dioxane XVIII arises by rearrangement of carbonium ion XX in the manner indicated below.

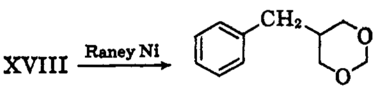


XX

N.m.r. analysis of XVII showed a coupling constant of 3 c.p.s. for the benzylic proton suggesting a *cis*-B,C-ring juncture. Raney nickel desulfurization provided 4-phenyl-5-methyl-1,3-dioxane (XXI) in 57% yield. Coupling of the C-4 proton with the C-5 proton in XXI was also 3 c.p.s. giving added evidence that the ring juncture in XVII was actually *cis*. The B,C-ring juncture of compound XVIII also appears



XXI



XXII

to be *cis* by virtue of the low coupling constant (J = 3 c.p.s.) for the 2-methine proton. In this case, desulfurization gave an 89% yield of 5-benzyl-1,3-dioxane (XXII) thus proving the skeletal structure of XVIII but not the stereoaspects of the B,C-ring juncture.

It is very possible that in solution formaldehyde is in equilibrium with its polymeric forms. Attack of the

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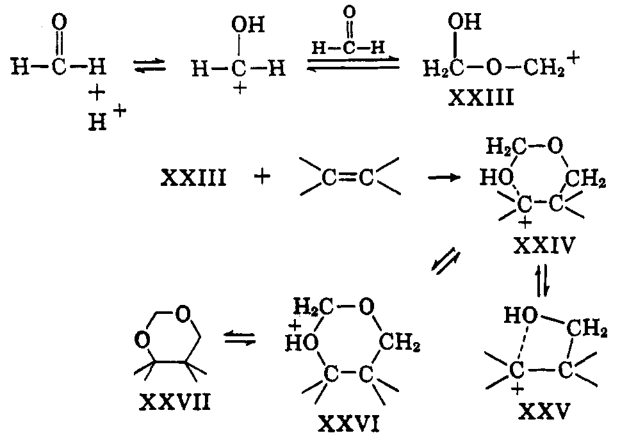
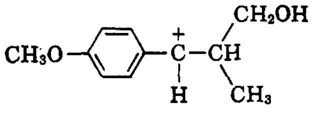
[13] F. W. Brugman and J. F. Arens, *Rec. trav. chim.*, **74**, 209 (1955).

[14] M. G. J. Beets and H. van Essen, *ibid.*, **71**, 343 (1952).

[15] W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

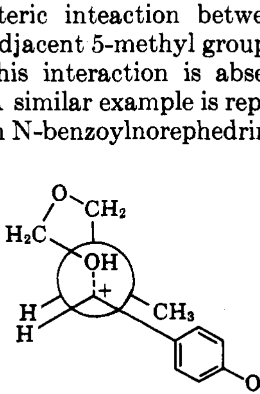
dimeric form XXIII on an olefin with subsequent stabilization of the so-formed carbonium ion, through a six-membered oxygen bridge rather than the four-membered system XXV[3-5] originally proposed, would lead to a highly stabilized intermediate XXIV. Backside attack of water on XXIV would still lead to *trans*-1,3-glycols, while carbon–oxygen bond formation followed by proton loss leads to *cis*-1,3-dioxanes XXVII. Equilibration of XXVII and XXIV may occur by protonation of the benzylic oxygen XXVI followed by carbon–oxygen bond cleavage to form XXIV. It is also possible to visualize a two-step addition process whereby formaldehyde adds to the oxygen of XXV and proceeds to XXIV. This would explain the conversion of both diols Va and Vb to the *m*-dioxane IIIa. The same carbonium ion, XXVIII, would be involved in both conversions. Carbonium ion XXVIII is readily formed in dilute acid as is shown by the rapid isomerization of diol Va.



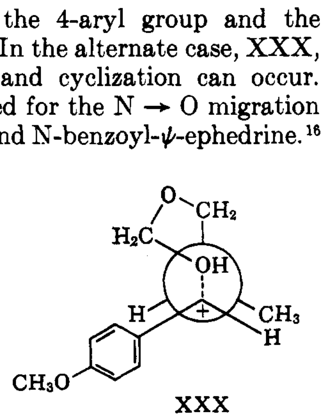


XXVIII

If product development control is invoked and the transition states for the two possible isomers are examined, it can be noted in XXIX that there is serious steric inteaction between the 4-aryl group and the adjacent 5-methyl group. In the alternate case, XXX, this interaction is absent and cyclization can occur. A similar example is reported for the N → O migration in N-benzoylnorephedrine and N-benzoyl-ψ-ephedrine.[16]



XXIX

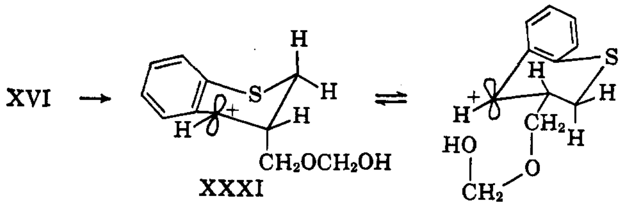


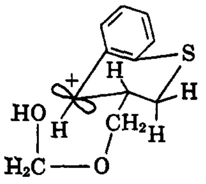
XXX

In acid the latter is rapidly converted to the O-benzoyl derivative, whereas the former remains unchanged. Eclipsed phenyl and methyl groups in the transition state account for the inactivity of the ephedrine derivative.[17] Logically, product development control can be extended to the cinnamic acid and isosafrole systems to explain the formation of the *trans* isomer as the kinetically controlled product.

Goering and Josephson[18] have noted that, with *cis*- and *trans*-5-methyl-2-cyclohexenol, the preferred geometry for rupture of allylic bonds is that in which the bond is perpendicular (quasi-axial) to the double bond. This geometry allows maximum overlap of the developing p-orbital with the π-orbital and subsequent formation of the allylic cation. A quasi-equatorial bond can attain this geometry only with considerable distortion of the ring, and is thus energetically less favored. It was further noted[18] that, from the principle of microscopic reversibility, quasi-axial bond formation on 5-methyl-2-cyclohexenol-1-yl carbonium ion should be preferred over quasi-equatorial.

If it is assumed that benzylic carbonium ions of tetralin (or derivatives thereof) have stereoelectronic requirements similar to the 2-cyclohexen-1-yl system, then quasi-axial attack should also be preferred. Such attack would explain the production of *cis* isomers as the products of a kinetically controlled process from the Prins reaction on the aromatic cyclic olefins. Thus, with 2H-1-benzothiopyran (XVI) one may envision axial attack on C-3 by either mono- or dimeric formaldehyde yielding ion XXXI followed by ring flip to give XXXII which now allows oxygen–carbon bond formation into the axial position of C-4. Formation of the *trans* isomer, XXXIII, requires bond formation with the incipient equatorial position. If the benzylic carbonium ion is to maintain maximum delocalization during bond formation, then the ring must undergo considerable distortion and is thus energetically unfavorable.





XXXIII

Thermodynamic control (in the case of anethole) necessitates reversal of *m*-dioxane IIIa to IV followed by rotation of C-4 and formation of IIIb. Since no isomeric pairs were observed in any of the systems, it must be concluded that reversal does not occur and that the *m*-dioxanes from aromatic olefins are formed primarily by a kinetically controlled process. Furthermore, cases have been reported[4,18,19] in which hydrolysis of the *m*-dioxanes to the glycols proceeds with retention of configuration at C-4, implying that

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(16) G. Fodor, V. Bruckner, J. Kiss, and G. Ohegyi, *J. Org. Chem.*, **14**, 337 (1949).

(17) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 145.

(18) H. L. Goering and R. R. Josephson, *J. Am. Chem. Soc.*, **84**, 2779 (1962).

(19) N. A. LeBel, R. N. Liesemer, and E. Mehmedbasich, *J. Org. Chem.*, **28**, 615 (1963).

bond cleavage occurs between C-2 and O-3 and that in hydrolysis species such as IV are not important. However, acetolysis of *m*-dioxane I afforded a mixture of diacetates.[6] This observation can be attributed to the rapid isomerization of the initially formed product.

Experimental[20]

Preparation of 4-Anisyl-5-methyl-1,3-dioxane (I).—The reaction of anethole with formaldehyde in glacial acetic acid was performed according to the method of Portoghese and Smissman[6] and gave a 25% yield of I, b.p. 93° (0.12 mm.), n^{20}_{D} 1.5338 [lit. b.p. 144–146° (0.7 mm.), n^{26}_{D} 1.4976].

Preparation of 1-Anisyl-2-methyl-1,3-propanediol (Va and Vb).—The diols Va and Vb were prepared by the hydrolysis of the diacetates IIa and IIb according to the directions of Portoghese and Smissman[6]; Va m.p. 62–63°, Vb m.p. 87–89° (lit. Va m.p. 62–63°, Vb m.p. 87–89°).

***cis*-4-Anisyl-5-methylpropylene Carbonate (VIa).**—Into a 300-ml. three-neck round-bottom flask equipped with a mechanical stirrer, condenser, and gas delivery tube was placed 5.88 g. (0.03 mole) of diol Va, 5 ml. of pyridine, and 150 ml. of dry ether. The system was cooled in an ice bath (*ca.* 5°) while a slow stream of phosgene, first passed through a cottonseed oil trap, was bubbled into the reaction flask. The solution turned cloudy (pyridine salts) followed by the formation of a dense white precipitate. After 4 hr. the reaction was terminated and for 0.5 hr. the system was purged with nitrogen. The ethereal solution was washed with 5% hydrochloric acid and water and dried; the solvent was removed. The oily residue was chromatographed on Florisil and elution with chloroform afforded an impure crystalline mass which on recrystallization from carbon tetrachloride gave 1.64 g. (25%) of colorless plates: m.p. 84–85°; infrared ($CHCl_3$) 5.71, 6.17, 6.57, 7.95, 8.45, 8.81, 9.62, and 11.99 μ; n.m.r. δ 7.09 (4 aromatic H), 5.65 (1 benzylic H, J = 3 c.p.s.), and 0.85 (3 methyl H).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 64.85; H, 6.35; mol. wt., 222.22. Found: C, 64.50; H, 6.01; mol. wt., 226.

***trans*-4-Anisyl-5-methylpropylene Carbonate (VIb).**—Diol Vb (1.27 g., 0.0065 mole) in the presence of 130 ml. of ether and 5 ml. of pyridine was treated with phosgene in the same manner as Va. After 1 hr. a dense white precipitate formed and the reaction was stopped, purged with nitrogen, washed with 5% hydrochloric acid and water and dried; the solvent was removed. The oily residue was chromatographed on Florisil, and elution with chloroform afforded an impure crystalline mass which, on recrystallization from ether-carbon tetrachloride, gave 250 mg. (17%) of colorless plates: m.p. 75–76.5°; infrared ($CHCl_3$) 5.72, 6.20, 6.60, 7.09, 7.97, 8.47, 8.79, 8.90, and 12.10 μ; n.m.r. δ 7.12 (4 aromatic H), 4.98 (1 benzylic H, J = 10 c.p.s.), and 0.82 (3 methyl H).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 64.85; H, 6.35; mol. wt., 222.22. Found: 64.81; H, 6.56; mol. wt., 221.

Preparation of 4-(3,4-Methylenedioxyphenyl)-5-methyl-1,3-dioxane (VII).—The preparation of VII was carried out by the procedure of Drukker and Beets[12]; n^{21}_{D} 1.5398 (lit. n^{20}_{D} 1.5404).

Preparation of 4-Phenyl-5-carboxy-1,3-dioxane (VIII).—The reaction of *trans*-cinnamic acid with paraformaldehyde was performed utilizing the method of Brugman and Arens[13] to give crude VIII. Several recrystallizations from carbon tetrachloride-petroleum ether gave tiny needles: m.p. 88.5–90°; n.m.r. δ 7.22 (5 aromatic H), 5.00 and 4.61 (2 pairs of doublets, 2 methylenedioxy H), and 4.60 (1 benzylic H, J = 10 c.p.s.).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.80. Found: C, 63.39; H, 5.82.

Reaction of 7-Methoxy-1,2-dihydronaphthalene (IX) with Formaldehyde in Glacial Acetic Acid.—Over a period of 2 hr. a slow stream of gaseous formaldehyde was passed into a mixture of 10 g. (0.063 mole) of 7-methoxy-1,2-dihydronaphthalene and 90 ml. of glacial acetic acid maintained at 90°. After continued heating at 90° for 3.5 hr., the mixture was allowed to cool to room temperature and the liquid was separated from the paraformaldehyde by centrifugation. The paraformaldehyde residue was mixed with a portion of ethyl acetate and centrifuged. The ethyl acetate was combined with the glacial acetic acid extract and the entire mixture was concentrated to a small volume *in vacuo*. The extract was washed several times with aqueous 5% sodium bicarbonate and dried over anhydrous magnesium sulfate; the solvent was removed under reduced pressure. The oil was distilled at 114–120° (0.03 mm.) giving approximately 1 ml. of viscous liquid; on prolonged standing a crystalline material was obtained. Several recrystallizations from ethanol gave large crystals of the *m*-dioxane X: m.p. 72–73°; infrared 3.65, (C–H stretching of $-O-CH_2-O-$), 8.00, 8.51, and 9.69 μ; n.m.r. δ 6.30 to 7.20 (3 aromatic H), 4.85 and 4.75 (two pairs of doublets, methylenedioxy), and 4.42 (1 benzylic H, J = 3 c.p.s.).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.21; H, 7.45.

Preparation of 2-Hydroxymethyleneindanol-1-formaldehyde Acetal (XI).—The reaction of indene with aqueous formaldehyde according to the method of Beets and van Essen[14] gave XI in 37% yield, b.p. 98–104° (0.7 mm.), lit. b.p. 117–125° (3 mm.).

Reaction of Coumarin (XII) with Formaldehyde in Glacial Acetic–Sulfuric Acids.—Coumarin (11.67 g., 0.08 mole), paraformaldehyde (12.5 g., 0.41 mole), and concentrated sulfuric acid (45 g.) were added to 150 ml. of glacial acetic acid and the well-stirred mixture was heated on a steam bath (90°) for 5 hr. after which the dark brown solution was cooled and poured into 400 g. of ice–water. A brown oily residue separated and was extracted with ether. The organic phase was washed several times with water, several times with 5% sodium bicarbonate, and again with water, and dried, and, on removal of solvent, 17.41 g. of a light yellow oil was obtained. Gas-liquid chromatography indicated a 74.7% yield of the coumarin methyl acetate XV, and no other Prins product. There was present in the mixture 5% of unchanged coumarin, and about 20% of paraformaldehyde and methylene diacetate. On standing, the oil crystallized and, after several recrystallizations from carbon tetrachloride, brilliant plates were obtained: m.p. 107–109°; infrared ($CHCl_3$) 5.80 (broad), 6.10, 6.21, 8.20 (broad), and 9.76 μ; n.m.r. δ 7.80 (1 olefinic H), 7.40 (4 aromatic H), 5.10 (2 methylene H), and 2.19 (3 methyl H).

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.04; H, 4.62. Found: C, 66.07; H, 4.73.

Preparation of 2H-1-Benzothiopyran (XVI).—The procedure of Parham[15] was used and a 91% yield of XVI was obtained, b.p. 78° (0.6 mm.), lit. b.p. 86–87° (0.85 mm.).

Reaction of 2H-1-Benzothiopyran (XVI) with Formaldehyde in Dilute Sulfuric Acid.—To a well-stirred mixture of 700 ml. of 40% formaldehyde solution (9.3 moles) and 18.3 g. of sulfuric acid, 86.36 g. (0.526 mole) of 2H-1-benzothiopyran was slowly added; the heterogeneous mixture was heated on a steam bath for 5 hr. after which the organic phase attained a light yellow color. The system was cooled, extracted with ether, washed with water, and dried; the solvent was removed. The oily residue was chromatographed on 1000 g. of silicic acid and eluted with chloroform; 300-ml. fractions were taken and analyzed by g.l.c. and n.m.r. 2H-1-Benzothiopyran (30 g.) was eluted first, followed by 11.2 g. of *m*-dioxane XVIII, 22.2 g. of a mixture of XVII and XVIII (1:1.85), and 15.7 g. of *m*-dioxane XVII; total yield was XVIII, 23.4%, and XVII, 21.5%. The latter, more polar fractions consisted of a complex mixture of alcoholic and carbonyl-containing compounds which were not identified.

An analytical sample of XVIII was prepared by distillation of the column eluate: b.p. 121–126° (0.30 mm.); n^{20}_{D} 1.6044; infrared ($CHCl_3$) 3.59 (C–H stretching of $-O-CH_2-O-$), 8.20, 8.52, 9.35, and 11.03 μ; n.m.r. δ 6.92 (4 aromatic H), 5.16 (2-methine H, J = 3 c.p.s.), and 4.95 and 4.55 (two pairs of doublets, 2 methylenedioxy H).

Anal. Calcd. for $C_{11}H_{12}O_2S$: C 63.43; H, 5.80; S, 15.39. Found: C, 63.76; H, 5.68; S, 14.87.

An analytical sample of XVII was prepared by distillation of the column eluate, b.p. 124–130° (0.4 mm.). On standing the yellow oil crystallized and, after two recrystallizations from ether–carbon tetrachloride, colorless needles were obtained: m.p. 95–96°; infrared ($CHCl_3$) 3.61 (C–H stretching of $-O-CH_2-O-$), 8.52, 9.79, and 10.25 μ; n.m.r. δ 7.00 (4 aromatic H), 4.90 and 4.65 (two pairs of doublets, 2 methylenedioxy H), and 4.42 (1 benzylic H, J = c.p.s.).

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(20) Melting points were obtained on a calibrated Thomas-Hoover Unimelt and are corrected. Infrared data were recorded on Beckman IR5 and IR8 spectrophotometers. N.m.r. data were recorded on a Varian Associates Model A-60 spectrophotometer using tetramethylsilane as the internal standard. Gas chromatographic data were obtained on F and M Models 500 and 810. Microanalyses were conducted by Drs. G. Weiler and F. B. Strauss, Oxford, England, and Huffman Microanalytical Laboratories, Wheatridge, Colo.

Anal. Calcd. for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.80; S, 15.39. Found: C, 63.15; H, 5.82; S, 15.45.

Desulfurization of *m*-Dioxane XVII to *cis*-4-Phenyl-5-methyl-1,3-dioxane (XXI).—Freshly prepared W-6 Raney nickel (85 g.) was slowly added to 6.12 g. (0.029 mole) of *m*-dioxane XVII and 300 ml. of dry benzene. After stirring for 4 hr. at room temperature, the benzene solution was decanted from the Raney nickel and the catalyst was washed several times with benzene. Evaporation of the solvent gave 5.63 g. of a yellow oil; g.l.c. analysis indicated a 57.5% yield of XXI.

An analytical sample was obtained by preparative g.l.c.: $n^{20}D$ 1.5235; infrared (liquid film) 3.60 (C–H stretching of –O–CH$_2$–O–), 8.50, 9.62, 9.85, 13.70, and 14.30 μ; n.m.r. δ 7.20 (5 aromatic H), 5.12 and 4.70 (two pairs of doublets, 2 methylenedioxy H), 4.68 (1 benzylic H, J = 3 c.p.s.), and 0.85 (3 methyl H).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.12; H, 7.91. Found: C, 73.85; H, 8.09.

Desulfurization of *m*-Dioxane XVIII to 5-Benzyl-1,3-dioxane (XXII).—To the well-stirred solution of *m*-dioxane XVIII (4.61 g., 0.022 mole) and 300 ml. of dry benzene was added 50 g. of freshly prepared W-6 Raney nickel. After 2 hr. of stirring at room temperature the benzene solution was decanted from the catalyst and the catalyst was washed several times with benzene. Evaporation of the solvent gave 3.95 g. of a colorless oily residue. Analysis by g.l.c. indicated an 89% yield of XXII. An analytical sample was obtained by preparative g.l.c.: $n^{20}D$ 1.5249; infrared (liquid film) 3.60 (C–H stretching of –O–CH$_2$–O–), 8.60, 9.71, 10.70, and 14.38 μ; n.m.r. δ 7.18 (4 aromatic H), 4.83 and 4.60 (two pairs of doublets, 2 methylenedioxy H), and 2.50 (2 benzylic H).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.12; H, 7.91. Found: C, 74.38; H, 8.03.

Attempted Isomerization of 2H-1-Benzothiopyran (XVI) to 4H-1-Benzothiopyran (XIX).[15]—Olefin XVI (1.36 g., 0.009 mole) was added to 150 ml. of water acidified with 70 drops of concentrated sulfuric acid. The mixture was heated on a steam bath for 5 hr. with stirring. After cooling, chloroform extraction, washing, drying, and solvent removal, 1.04 g. (76.5%) of a red oil was obtained whose n.m.r. was identical with that of XVI.

Reaction of 1-Anisyl-2-methyl-1,3-propanediol (Va) with Aqueous Formaldehyde.—Diol Va (1.0 g., 0.005 mole) was heated on a steam bath with 30 ml. of aqueous 37% formaldehyde for 24 hr. The solution was cooled, extracted with ether, washed with water, and dried. The oil which remained after solvent removal exhibited an infrared spectrum which was superimposable with the *m*-dioxane prepared in acetic acid.[6]

Reaction of 1-Anisyl-2-methyl-1,3-propanediol (Vb) with Aqueous Formaldehyde.—Diol Vb (1.0 g., 0.005 mole) was treated in a manner similar to the procedure above. The *m*-dioxane which was formed had an infrared spectrum identical in all respects with that prepared from diol Va and with that prepared by the acetic acid method.[6]

Reaction of 1-Anisyl-2-methyl-1,3-propanediol (Va) with Dilute Formic Acid.—Diol Va (0.670 g.) was heated on a steam bath in 30 ml. of 0.02 *M* formic acid for 5 hr. The solution was cooled, extracted with ether, and dried. On removal of solvent, 0.660 g. of a clear oil remained whose n.m.r. indicated a 1:1 mixture of diol Va and Vb. No attempt was made to establish complete equilibrium.

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Solvolyses of 1,1-Diphenyl-2-haloethanols and of 1,1-Diphenylethylene Oxide. Thermal Behavior of the Epoxide and Its Reactions with Phenylmagnesium Bromide and with Phenyllithium[1]

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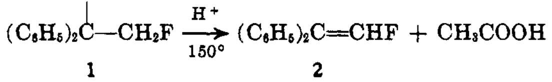
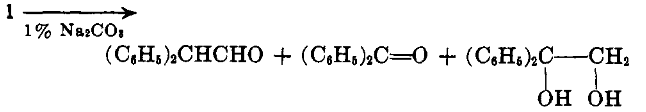
Solvolysis of a series of 1,1-diphenyl-2-haloethanols in dioxane–water containing 1% sodium carbonate gave 1,1-diphenylethylene glycol and, unexpectedly, diphenylacetaldehyde and benzophenone. The intermediacy of 1,1-diphenylethylene oxide (**6**) is proposed to explain the formation of these products. Support for this explanation was obtained from investigations of the thermal isomerization of **6** and of the solvolysis of **6** in dioxane–water at pH values ranging from 2.7 to 13.0. In addition, a comparative analysis of the products from the action of phenylmagnesium bromide and of phenyllithium on the epoxide is described. Whereas the reaction of the epoxide with the Grignard reagent afforded 1,2,2-triphenylethanol (**9**) as the sole carbinol, the reaction with phenyllithium gave both **9** and its isomer, 1,1,2-triphenylethanol (**10**). Mechanistic implications of these results and their significance in the light of certain previously reported observations are discussed.

In a previous publication[2] the preparation of 1,1-diphenyl-2-fluoroethyl acetate (**1**) and its acid-catalyzed pyrolysis to 1,1-diphenyl-2-fluoroethylene (**2**) in 84% yield were described. Recently we have observed that, whereas solvolysis of acetate **1** in a 1:1 mixture of dioxane–water at reflux temperature for 24 hr. regenerated the progenitor, 1,1-diphenyl-2-fluoroethanol (**3**), in 56% yield, solvolysis of **1** in aqueous dioxane containing 1% sodium carbonate afforded none of the fluorocarbinol **3**. The reaction product consisted mainly of diphenylacetaldehyde and benzophenone and of comparatively smaller amounts of 1,1-diphenylethylene glycol (**7**) and polymeric material.[3] In the light of these unexpected results, an investigation of the reaction pathway seemed appropriate.



$$\underset{\mathbf{1}}{(C_6H_5)_2\overset{\overset{\displaystyle OCOCH_3}{|}}{C}{-}CH_2F} \xrightarrow[150°]{H^+} \underset{\mathbf{2}}{(C_6H_5)_2C{=}CHF} + CH_3COOH$$



$$\mathbf{1} \xrightarrow[1\%\ Na_2CO_3]{dioxane\text{-}H_2O} (C_6H_5)_2CHCHO + (C_6H_5)_2C{=}O + \underset{\mathbf{7}}{(C_6H_5)_2\underset{\underset{\displaystyle OH}{|}}{C}{-}\underset{\underset{\displaystyle OH}{|}}{CH_2}}$$

Since the solvolysis of 1,1-diphenyl-2-fluoroethyl acetate (**1**) in dioxane–water gave the corresponding alcohol **3**, it appeared likely that **3** was undergoing

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[2] J. Bornstein, M. R. Borden, F. Nunes, and H. I. Tarlin, *J. Am. Chem. Soc.*, **85**, 1609 (1963).

[3] Analytical tools used in this investigation were infrared spectroscopy and gas, column, and thin layer chromatography. The carbonyl components of the reaction mixtures were isolated and characterized at various times as the 2,4-dinitrophenylhydrazine derivatives (*cf.* Experimental section).