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.

Acknowledgment.—The authors gratefully acknowledge the support of this project by the National Science Foundation Grant GP-190.

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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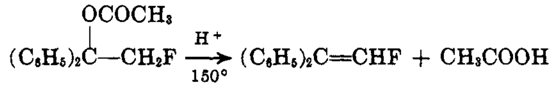
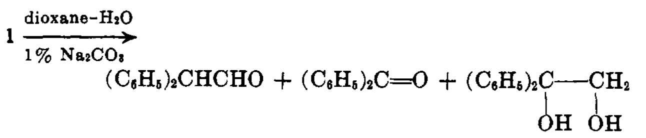
Solvolysis of a series of 1,1-diphenyl-2-haloethanols in dioxane–water containing 1% sodium carbonate gave 1,1-diphenylethylene glycol and, unexpectedly, diphenylacetaldehyde and benzophenone. The intermediacy of 1,1-diphenylethylene oxide (**6**) is proposed to explain the formation of these products. 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.



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



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

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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(1) Supported in part by a research grant (NSF-G22020) from the National Science Foundation.

(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).

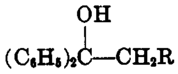
TABLE I

EFFECT OF pH AND TEMPERATURE ON YIELDS OF PRODUCTS FROM SOLVOLYSES OF VARIOUS COMPOUNDS IN AQUEOUS DIOXANE[a]

Run	Compd., mg. (mmoles)	Added solute (mg.)	pH	Temp., °C.	Crude product, mg.	Yields, %[b]		
						Ph_2CHCHO[c]	Ph_2CO[c]	$Ph_2C(OH)-CH_2OH$[d]
1	1,1-Diphenyl-2-fluoroethyl acetate,							
	500 (1.94)	Na_2CO_3 (300)	11.3	88 (reflux)	361	18	21	21
2	500 (1.94)	. . .	~5.5	88 (reflux)	303[e]	0	0	0
3	1,1-Diphenyl-2-fluoroethanol,							
	418 (1.93)	Na_2CO_3 (300)	11.3	88 (reflux)	356	21	18	22
4	418 (1.93)	. . .	~5.5	88 (reflux)	407[f]	0	0	0
5	418 (1.93)	p-$CH_3C_6H_4SO_3H$ (6)	2.7	88 (reflux)	427[g]	0	0	0
6	1,1-Diphenyl-2-chloroethanol,							
	450 (1.93)	Na_2CO_3 (300)	11.3	88 (reflux)	358	23	21	22
7	1,1-Diphenyl-2-bromoethanol,							
	535 (1.93)	Na_2CO_3 (300)	11.3	88 (reflux)	363	19	19	21
8	1,1-Diphenylethylene oxide,							
	500 (2.55)	NaOH (115)	13.0	88 (reflux)	438[h]	5	10	53
9	250 (1.28)[i]	NaOH (115)	13.0	50	232[j]	<1	7	9
10	500 (2.55)	Na_2CO_3 (300)	11.3	88 (reflux)	466	16	20	25
11	200 (1.02)	Na_2CO_3 (300)	11.3	88 (reflux)	181	16	20	19
12	200 (1.02)[i]	Na_2CO_3 (300)	11.3	50	176[k]	<1	4	<1
13	500 (2.55)	. . .	~5.5	88 (reflux)	430[l]	12	<2	85
14	500 (2.55)	. . .	~5.5	50	480[m]	<3	<2	94
15	500 (2.55)	p-$CH_3C_6H_4SO_3H$ (6)	2.7	88 (reflux)	455[m]	10	<1	90
16	500 (2.55)	p-$CH_3C_6H_4SO_3H$ (6)	2.7	50	470[n]	<2	<1	97

[a] In each run, 30 ml. of a 1:1 mixture of dioxane–water, b.p. 88°, was used. All runs were carried out at the stated temperature for 24 hr., and the reaction mixture was then allowed to stand at room temperature an additional 24 hr. before being worked up. Unless otherwise noted, the products were oils. [b] Percentages are for the composition of the crude reaction product and are average values from two or more runs. [c] Quantitatively determined by infrared analysis in carbon tetrachloride. [d] Quantitatively determined either by direct isolation and/or by infrared spectroscopy in carbon tetrachloride. In those cases where the glycol was the major product, the spectrum was measured in chloroform. [e] 1,1-Diphenyl-2-fluoroethanol was isolated in 56% yield by crystallization of the solid crude product from hexane; m.p. 71–72° (lit.[5] m.p. 71.8–72.6°). [f] Unchanged starting fluorohydrin. [g] Starting compound containing dioxane (possibly a solvate), m.p. 88–91.5°. Sublimation at 70° (1 mm.) or recrystallization from carbon tetrachloride gave the pure fluorohydrin in 85% yield, m.p. 72–73°. The suspected solvate was subsequently prepared by crystallizing pure 1,1-diphenyl-2-fluoroethanol from dioxane; its infrared spectrum and melting point were identical with those of the crude product obtained from this attempted solvolysis. [h] Oily solid. [i] Owing to the combination of lower temperature and added solute it was necessary to use less than the usual amount of epoxide in order to obtain a homogeneous solution. [j] White solid, m.p. 43–53°, mainly unchanged starting epoxide. [k] White solid, m.p. 51–54°, mainly unchanged epoxide. [l] White solid, m.p. 110–117°, raised to 120–121° after one recrystallization from water. Infrared analysis and a mixture melting point showed this material to be 1,1-diphenylethylene glycol (lit.[9] m.p. 120–121°). [m] White solid, m.p. 111–119°. [n] White solid, m.p. 118–122°.

further reaction when alkali was present to produce the mixture of compounds noted above. This possibility was confirmed by subjecting 1,1-diphenyl-2-fluoroethanol[2] (3) to solvolysis in dioxane–water–sodium carbonate at reflux temperature; practically the same amounts of diphenylacetaldehyde, benzophenone, and 1,1-diphenylethylene glycol (7) were formed (Table I). The solvolysis was subsequently repeated with 1,1-diphenyl-2-bromoethanol[4] (4) and 1,1-diphenyl-2-chloroethanol[5] (5) and in both these cases the results were similar to those realized with the fluoro analog (Table I). These observations indicated that a common intermediate must be involved in the conversion of the halohydrins to the mixture of aldehyde, ketone, and glycol. In view of the ability of halohydrins to form epoxides on treatment with base,[6] 1,1-diphenylethylene oxide, which is well known to rearrange under certain conditions to diphenylacetaldehyde,[7–10] was suspected as this intermediate.



$$(C_6H_5)_2\overset{\overset{OH}{|}}{C}{-}CH_2R$$

3, R = F
4, R = Br
5, R = Cl

Accordingly, a study at reflux temperature of the solvolysis of 1,1-diphenylethylene oxide (6) in dioxane–water at pH values[11] of 11.3, ~5.5, and 2.7 was made. The results strongly suggest that 6 is the reaction intermediate in the solvolysis of the halohydrins. Thus, the solvolysis of 1,1-diphenylethylene oxide (6) in aqueous dioxane containing 1% sodium carbonate (pH 11.3, runs 10 and 11) afforded a mixture of products which was strikingly similar in composition to the mixtures obtained earlier from the halohydrins under the same experimental conditions (Table I). A control experiment established that the rearrangement of the epoxide to diphenylacetaldehyde was occurring during the solvolysis and not during the course of isolation of the products. On the other hand, the solvolysis of 1,1-diphenylethylene oxide (6) in aqueous

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(4) S. J. Cristol, J. R. Douglass, and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 816 (1951).

(5) E. F. Silversmith and D. Smith, *J. Org. Chem.*, **23**, 427 (1958).

(6) S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. I, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 8.

(7) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(8) A. Klages and J. Kessler, *Ber.*, **39**, 1754 (1906).

(9) G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, 247 (1945).

(10) A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).

(11) The pH values throughout this paper are for water (pH ~5.5) and aqueous solutions of p-toluenesulfonic acid, sodium carbonate, and sodium hydroxide, free of dioxane and other organic solutes. For a discussion of the difficulties inherent in attempts to attach significance to pH measurements of aqueous solutions containing substantial quantities of organic solutes, *cf.* V. Gold, "pH Measurements," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 104.

dioxane (pH ~5.5, run 13) and in aqueous dioxane containing a small quantity of *p*-toluenesulfonic acid (pH 2.7, run 15) yielded in both instances 1,1-diphenylethylene glycol (7) as the major product; diphenylacetaldehyde and benzophenone were formed in only small amounts. Evidence that 1,1-diphenylethylene glycol (7) was not the source of the diphenylacetaldehyde and the benzophenone was obtained by treating glycol 7 with dioxane–water–sodium carbonate under conditions that caused the simultaneous rearrangement and hydration of epoxide 6; the glycol was recovered intact. Deoxybenzoin, which like diphenylacetaldehyde is a possible product of rearrangement of 1,1-diphenylethylene oxide (6),[10] was then subjected to the same solvolytic conditions. Again, no reaction occurred and deoxybenzoin was recovered quantitatively.

Although the foregoing experiments demonstrate the intermediacy of 1,1-diphenylethylene oxide (6) in the solvolysis of the halohydrins under basic conditions they furnished no clue to the cause of the rearrangement of 6 to the aldehyde. There are no reports in the literature of the base-catalyzed rearrangement of epoxide 6 to diphenylacetaldehyde; this isomerization has, however, been effected both thermally[8,9] and with acid catalysts.[10] Cope, Trumbull, and Trumbull[10] who purposely attempted to effect a base-catalyzed epoxide–carbonyl rearrangement of 6 with lithium diethylamide in refluxing ether found no evidence of rearrangement and observed only ring opening with normal addition. Likewise, Cristol, Douglass, and Meek[4] observed only ring opening with normal addition in their study of the reaction of ethereal phenyllithium with 1,1-diphenylethylene oxide (6) (however, *vide infra*). Although the findings of these investigators[4,10] indicated that the isomerization of 6 observed by us in dioxane–water–sodium carbonate was almost certainly the result of heating and not of base catalysis, our reaction conditions were so different from theirs that further investigation of the nature of the rearrangement seemed warranted. Accordingly, 1,1-diphenylethylene oxide (6) was solvolyzed (runs 8 and 9) in aqueous dioxane containing sodium hydroxide at reflux temperature and at 50° under more strongly basic conditions (pH 13.0) than had been used previously. In addition, the three solvolyses that had been carried out earlier at pH 11.3, ~5.5, and 2.7 at reflux temperature (runs 11, 13, and 15, respectively) were repeated at 50° (runs 12, 14, and 16, respectively). The results of these experiments are summarized in Table I.

In general, the data in Table I are consistent with a thermal mechanism for the rearrangement of epoxide 6. Thus, solvolyses 8–16, carried out at both reflux temperature and 50°, show that at any given pH value, smaller amounts of diphenylacetaldehyde and benzophenone are formed at the lower temperature. However, since both hydration and rearrangement of 6 occur to a significant degree during the solvolysis of the epoxide, especially under basic conditions, it was felt that evidence of a more decisive nature in support of a thermal mechanism might be obtained by studying the isomerization of 6 under conditions which were free of the competing glycol-forming reaction. Therefore, the effect of heat on 1,1-diphenylethylene oxide (6) under anhydrous conditions was examined. The isomerization was investigated in anhydrous dioxane, in anhydrous benzene, and also in the absence of solvents at several temperatures. The results are summarized in Table II. A notable feature of the data is that the combined yield of diphenylacetaldehyde and benzophenone formed from 6 in refluxing solvents is at least as great or greater than that produced during the solvolysis of 6 (Table I, runs 10 and 11). These data strongly indicate that the isomerization of 1,1-diphenylethylene oxide (6) occurs primarily by a thermal mechanism rather than by a base-catalyzed mechanism. The observations of Cope, Trumbull, and Trumbull[10] and of Cristol, Douglass, and Meek[4] discussed earlier lend support to this conclusion.

TABLE II

YIELDS OF DIPHENYLACETALDEHYDE AND BENZOPHENONE FROM THERMAL ISOMERIZATION OF 1,1-DIPHENYLETHYLENE OXIDE[a]

Solvent, ml.	Temp., °C.	Time, hr.	Diphenylacetaldehyde, %[b]	Benzophenone, %[b]
Dioxane, 3.0	101 (reflux)	24	38	9
Dioxane, 3.0	25	48	5	<1
Benzene, 3.0	80 (reflux)	24	35	5
None[c]	125	24	15	5
None[c]	125	10	8	<1
None[c]	125	2	<1	0
None[c]	200	2.5	97	3
None[d]	25	120	0	0
None[e]	25	120	23	20

[a] In each run, a 100-mg. quantity of epoxide, m.p. 55–56°, was used. [b] Percentage yields were determined by infrared analysis in carbon tetrachloride. Unless otherwise noted, the weight of recovered product ranged from 93 to 98 mg. [c] Heating of the epoxide was carried out in an atmosphere of dry nitrogen. [d] Sample was stored over phosphorus pentoxide and had m.p. 55–56° at the end of this time; after 1 month the melting point was still unchanged. [e] Sample was allowed to stand exposed to the atmosphere and at the end of the stated time it weighed 105 mg. Also present in this product was 55% of 1,1-diphenylethylene glycol.

A second interesting feature of the data in Table II is that under comparable conditions the isomerization of epoxide 6 is considerably faster in solvents than in their absence. The reason for this striking difference in rate is not known.

A clue to the origin of the benzophenone formed in the solvolyses of 1,1-diphenylethylene oxide was eventually furnished from infrared examination of a sample of diphenylacetaldehyde[12] which had been stored at room temperature for 3 years. The spectrum of this material revealed the presence of approximately 8% of benzophenone, which was conclusively identified by gas chromatography and by its isolation as the 2,4-dinitrophenylhydrazone. This observation suggested that the ketone produced in the solvolyses arose from oxidative cleavage of diphenylacetaldehyde. Evidence that this was the case was obtained from two experiments: (1) when a sample of diphenylacetaldehyde was subjected to solvolysis under the usual basic conditions, a significant amount of benzophenone was formed; and (2) exposure of a thin film of the aldehyde

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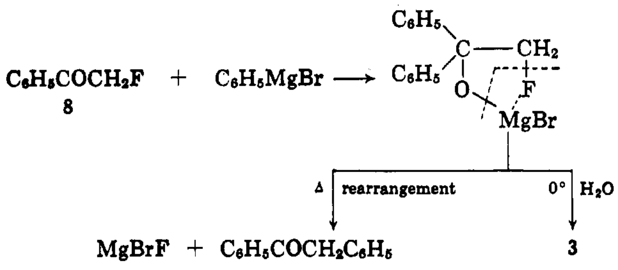
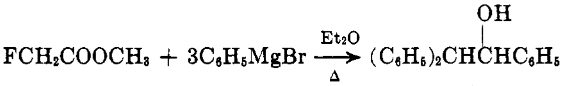
[12] Kindly furnished by Professor Herbert O. House.

to the atmosphere for 2 months led to the formation of benzophenone in 37% yield.[13]

The foregoing study of the halohydrins and of 1,1-diphenylethylene oxide called to mind certain contradictory observations made by Bergmann and Kalmus[14] and by Mirosevic-Sorgo and Saunders.[15] The former investigators had reported that the reaction of 1 mole of phenylmagnesium bromide with phenacyl fluoride (**8**) at the reflux temperature of ether yielded deoxybenzoin exclusively. On the other hand, when this reaction was carried out at 0° they obtained the expected product, 1,1-diphenyl-2-fluoroethanol (**3**). Their claim that only deoxbenzoin is produced at elevated temperature appeared questionable in the light of the report of Mirosevic-Sorgo and Saunders that the action of 3 moles of ethereal phenylmagnesium bromide on methyl fluoroacetate or fluoroacetyl chloride at reflux temperature afforded 1,2,2-triphenylethanol (**9**).[16]

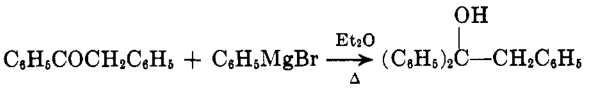




$$FCH_2COOCH_3 + 3C_6H_5MgBr \xrightarrow[\Delta]{Et_2O} (C_6H_5)_2CH\overset{OH}{\overset{|}{C}}HC_6H_5$$

9

Clearly, if only deoxybenzoin is formed as claimed by Bergmann and Kalmus then it might be expected that this ketone would react with the Grignard reagent to furnish 1,1,2-triphenylethanol (**10**),[17] which is an isomer of the carbinol **9** actually isolated by Mirosevic-Sorgo and Saunders.[18]



$$C_6H_5COCH_2C_6H_5 + C_6H_5MgBr \xrightarrow[\Delta]{Et_2O} (C_6H_5)_2\overset{OH}{\overset{|}{C}}—CH_2C_6H_5$$

10

Prompted by this apparent inconsistency, we have re-examined the action of 1 mole of phenylmagnesium bromide on phenacyl fluoride (**8**) at reflux temperature[14] and have found by column chromatography both deoxybenzoin (38% yield) and 1,2,2-triphenylethanol (**9**, 13% yield) among the reaction products. We believe the secondary carbinol **9** is produced from the reaction of the Grignard reagent with 1,1-diphenylethylene oxide (**6**),[19] which, like deoxybenzoin, can conceivably be formed *in situ* from the magnesium alkoxide of 1,1-diphenyl-2-fluoroethanol (**3**). Although we were unable to detect spectroscopically or chromatographically any epoxide in the crude reaction mixture, support for this pathway was obtained from an investigation of the reaction of phenylmagnesium bromide with 1,1-diphenylethylene oxide. Thus, when equimolar amounts of these reagents were refluxed in ether for 45 min., 1,2,2-triphenylethanol (**9**) was produced in 60% yield. Thin layer and column chromatographic analyses of the crude reaction product showed that none of the possible isomeric carbinols 1,1,2-triphenylethanol (**10**) and 2,2,2-triphenylethanol (**11**)[4] was present. The fact that diphenylacetaldehyde

$$(C_6H_5)_3C—CH_2OH$$

11

was found by infrared analysis to be present in the crude reaction mixture leads to the conclusion that under the influence of the Grignard reagent, 1,1-diphenylethylene oxide (**6**) first undergoes a typical epoxide-carbonyl rearrangement to the aldehyde, which then reacts further with the Grignard reagent to yield the secondary carbinol **9**. The authentic comparison sample of **9** was made in 64% yield by treating diphenylacetaldehyde with phenylmagnesium bromide.

For the purpose of comparison, we have re-examined the action of phenyllithium on 1,1-diphenylethylene oxide (**6**) in ether solution. This reaction had been studied previously by Cristol, Douglass, and Meek[4] before the advent of such sensitive analytical tools as gas and thin layer chromatography. These investigators had reported that 1,1,2-triphenylethanol (**10**), formed by nucleophilic displacement by the phenyl group of phenyllithium on the methylenic carbon atom of **6**, is the sole carbinol produced in this reaction. Our investigation has confirmed that the tertiary carbinol **10** is formed in the amounts claimed by these earlier workers but, in addition, we have found that at least 6% of the isomeric secondary carbinol, 1,2,2-triphenylethanol (**9**), accompanies **10**.[20] Whereas column chromatography on alumina of the crude reaction mixture gave **9** in only 2.4% yield, acetylation of the crude reaction mixture with acetic anhydride followed by crystallization of the resulting product conveniently afforded the acetate of **9** in yields of 6–7%, consistently.

Since as much as 8% of diphenylacetaldehyde was found by infrared analysis to be present in the crude, unchromatographed mixtures from the epoxide–phenyllithium reaction, it is certain that a small amount of epoxide **6** undergoes isomerization to the aldehyde, which subsequently must react with phenyllithium to yield 1,2,2-triphenylethanol (**9**). It is not known at this time what factors are responsible for promoting the isomerization, but it appears almost certain that the isomerization is not caused by the lithium bromide present in the ethereal solution of the organometallic reagent. Thus, treatment of **6** with a saturated ethereal solution of this salt at reflux temperature for

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[13] After we had completed this work, J. W. Huffman and R. P. Elliott [*Chem. Ind.* (London), 650 (1963)] described the base-catalyzed autoxidation of diphenylacetaldehyde to benzophenone.

[14] F. Bergmann and A. Kalmus, *J. Am. Chem. Soc.*, **76**, 4137 (1954).

[15] P. Mirosevic-Sorgo and B. C. Saunders, *Tetrahedron*, **5**, 38 (1959).

[16] There is no doubt about the intermediacy of phenacyl fluoride (**8**) in the reaction of the ester with the Grignard reagent since on several occasions we have isolated this ketone as a coproduct in the course of preparing **3** from phenylmagnesium bromide and ethyl fluoroacetate at lower temperature.

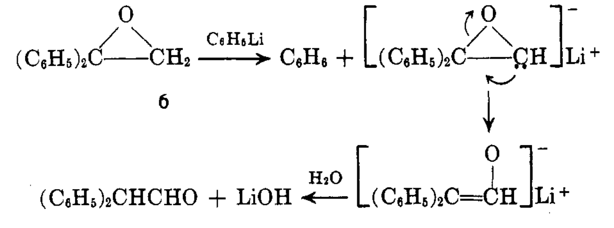
[17] A. Klages and S. Heilmann [*Ber.*, **37**, 1447 (1904)] have prepared **10** by this route.

[18] We are indebted to Dr. Saunders for a stimulating discussion of this point.

[19] *Cf.* J. S. W. Boyle, A. McKenzie, and W. Mitchell, *Ber.*, **70**, 2153 (1937); T. Ando, *Yuki Gosei Kagaku Kyôkai Shi*, **17**, 777 (1959); *Chem. Abstr.*, **54**, 4492*f* (1960).

[20] Infrared analysis and particularly thin layer chromatography readily demonstrated the presence of **9** in the crude reaction mixtures. Programmed gas chromatography (silicone gum rubber) proved to be of no practical use in this instance because both **9** and **10** underwent dehydration to triphenylethylene during attempted analysis.

2 hr. and also at room temperature for 24 hr. (the times and temperatures used in carrying out the reaction of 6 with phenyllithium) was without effect; the epoxide was recovered unchanged in quantitative yield from both attempts. It is possible that this isomerization is another example of a base-catalyzed rearrangement of an epoxide brought about in the present instance by the strongly basic organometallic reagent. If this is truly the case, the rearrangement probably proceeds *via* the same proton-abstraction mechanism proposed by Cope, Trumbull, and Trumbull[10] to explain the base-catalyzed epoxide–carbonyl rearrangement observed with other epoxides bearing more acidic hydrogen atoms.



Experimental[21]

The following typical examples illustrate the general procedures used to carry out the solvolyses. Any significant changes in these procedures are noted in Table I under each specific case.

Solvolysis of 1,1-Diphenyl-2-fluoroethyl Acetate (1) in Dioxane–Water–Sodium Carbonate (pH 11.3).—To a solution of 500 mg. of 1 in 15 ml. of dioxane was added a solution of 300 mg. of sodium carbonate in 15 ml. of distilled water. The resultant faintly cloudy mixture, which became clear and homogeneous on warming, was heated under reflux for 24 hr. and then allowed to stand at room temperature an additional 24 hr. The reaction mixture, which contained a small amount of suspended oil, was extracted twice with 100-ml. portions of ether and the combined colorless ether extracts were washed three times with 40-ml. portions of water and dried. Evaporation of the ether at reduced pressure at 25°, followed by further concentration of the crude product at reduced pressure at 75–85°, gave a straw-colored oil whose weight ranged from 347 to 375 mg. in four runs. The infrared spectrum of the oil (CCl_4 solution) displayed bands suggestive of the presence of diphenylacetaldehyde, benzophenone, and 1,1-diphenylethylene glycol. The presence of diphenylacetaldehyde and benzophenone was confirmed by gas chromatography; authentic samples of these compounds were used for comparisons of retention times. The ketone was eluted at 200° and elution of the aldehyde occurred at 207°. These carbonyl-containing components were further characterized by conversion to the corresponding 2,4-dinitrophenylhydrazones. A portion of the crude oil was treated with 2,4-dinitrophenylhydrazine reagent[22] and separation of the resulting mixture of dinitrophenylhydrazones was readily effected by extraction with boiling absolute ethanol in which solvent the derivative of diphenylacetaldehyde was considerably more soluble than that of benzophenone. The 2,4-dinitrophenylhydrazone of diphenylacetaldehyde, recrystallized twice from ethanol, had m.p. 151–152° (lit.[23] m.p. 150–151°) and was shown to be identical with an authentic specimen[12] by a mixture melting point determination and infrared spectral comparison. The identity of benzophenone 2,4-dinitrophenylhydrazone, m.p. 239–240° (twice recrystallized from glacial acetic acid) (lit.[24] m.p. 238–239°), was established in similar fashion. The percentage yields of diphenylacetaldehyde and benzophenone (summarized in Table I) were obtained by quantitative infrared analysis of 20- and 50-mg. aliquots of the crude oily product diluted to a volume of 1.0 ml. with CCl_4. The intensities of the absorption bands characteristic of the aldehyde at 3.63 and 5.82 μ and of the bands characteristic of the ketone at 6.02, 10.63, and 10.88 μ were compared with calibration curves obtained from the spectra of authentic samples (2, 5, 10, 20, 35, and 50 mg./ml. of CCl_4 solution) of these carbonyl-containing compounds.

Dilution of a 200-mg. quantity of the crude oily product with 1.0 ml. of CCl_4 followed by chilling at 0° for 3 days of the resulting solution gave 32 mg. of 1,1-diphenylethylene glycol as white needles, m.p. 118–120° (lit.[9] m.p. 120–121°). The substance was shown to be identical with an authentic sample[9] by infrared spectral comparison ($CHCl_3$ solution) and a mixture melting point determination. The percentage yields of glycol obtained by this method of isolation in four runs were consistently 20–30% lower than the percentage yields as determined by quantitative infrared analysis of the crude oil using the absorption band characteristic of the glycol at 2.77 μ (Table I). Chloroform was used as solvent for these spectrophotometric measurements (because of the low solubility of 1,1-diphenylethylene glycol in CCl_4) and the comparisons were made against a calibration curve obtained from an authentic sample of glycol at concentrations of 2, 5, 10, and 20 mg./ml. of solution.

The presence of a yellow, intractable gum (10–15%) in the crude oily product from the solvolysis was revealed by short-path distillation (95° at 1.0 mm.) of a portion of the oil; this operation removed the more volatile aldehyde, ketone, and glycol components.

Solvolysis of 1,1-Diphenyl-2-fluoroethyl Acetate (1) in Dioxane–Water (pH ~5.5).—After a mixture of 500 mg. of 1, 15 ml. of dioxane, and 15 ml. of distilled water had been heated under reflux 24 hr. and then allowed to stand at room temperature an additional 24 hr., it was worked up by the procedure described above. The crude product was a white solid (303 mg.) and afforded, after recrystallization from hexane, 234 mg. (56%) of 1,1-diphenyl-2-fluoroethanol, m.p. 71–72° (lit.[5] m.p. 71.8–72.6°), identical in all respects with an authentic sample.

Solvolysis of 1,1-Diphenylethylene Oxide (6) in Dioxane–Water–Acid (pH 2.7).—Sufficient *p*-toluenesulfonic acid monohydrate (*ca.* 6 mg.) was dissolved in 15 ml. of water to bring the solution to pH 2.7. To this solution were added in succession 15 ml. of dioxane and a 500-mg. quantity of 1,1-diphenylethylene oxide.[4] The resulting initially cloudy mixture was heated under reflux for 24 hr. and then allowed to stand an additional 24 hr. at room temperature. The reaction mixture was worked up following the procedure described above for the solvolysis of 1 in basic solution. The crude product was a white solid, m.p. 111–119°, and weighed 455 mg. (average value from three runs). Infrared analysis confirmed that this material was mainly 1,1-diphenylethylene glycol, contaminated (weak absorption at 5.82 and 6.02 μ) with small amounts of diphenylacetaldehyde and benzophenone.

Solvolysis of 1,1-Diphenylethylene Oxide (6) in Dioxane–Water–Sodium Hydroxide (pH 13.0) at 50°.—To 30 ml. of a 1:1 mixture of dioxane–water containing 115.4 mg. (2.83 mmoles) of sodium hydroxide was added 250 mg. of 1,1-diphenylethylene oxide. The resultant slightly cloudy mixture cleared on warming to 50° at which temperature it was held for 24 hr. and then allowed to stand at room temperature for an additional 24 hr. The reaction mixture was worked up in the usual way and afforded 232 mg. (average value from two runs) of a white solid, m.p. 43–53°. Infrared analysis showed that this material was composed of unchanged epoxide mainly, a trace of diphenylacetaldehyde, 7% of benzophenone, and 9% of 1,1-diphenylethylene glycol.

Control Experiments. A. 1,1-Diphenylethylene Oxide (6).—Evidence that the rearrangement of epoxide 6 to diphenylacetaldehyde had occurred during the course of solvolysis at pH 11.3 and was not caused by the method of isolation of the reaction product was obtained as follows. A solution of 100 mg. of 6 (m.p. 55–56°) in 3.0 ml. of dioxane was treated with a solution

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[21] Melting points are corrected. Thin layer chromatography was done with silica gel as adsorbent; iodine vapor was used to detect the various compounds. Gas chromatography was carried out on an F and M Model 500 gas chromatograph using a 2-ft. silicone gum rubber column with helium as the carrier gas. Infrared spectra were determined with either a Baird Model B spectrophotometer or a Perkin-Elmer Model 137 Infracord. A Corning pH meter, Model 12, was used for the pH measurements.[11] Sodium sulfate was employed as a drying agent. Spectroquality *p*-dioxane (Matheson Coleman and Bell) was used without further purification as solvent in the solvolyses. Elemental analyses were performed by Drs. S. M. Nagy, M.I.T., and Carol K. Fitz, Needham Heights, Mass.

[22] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 111.

[23] H. O. House, *J. Am. Chem. Soc.*, **77**, 3070 (1955).

[24] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Order I, John Wiley and Sons, Inc., New York, N. Y., 1941; p. 363.

of 60 mg. of sodium carbonate in 3.0 ml. of water. The resulting cloudy mixture was swirled for 2 min. at room temperature and then extracted with two 20-ml. portions of ether. The combined ether extracts were washed three times with 15-ml. portions of water and dried. Removal of the ether on the steam bath, followed by further concentration of the product under reduced pressure at 85–90°, gave a colorless oil, which rapidly crystallized when cooled. The solid (96 mg.) had m.p. 54–56° and was found by infrared analysis to be unchanged epoxide, completely free of any carbonyl-containing material.

B. **1,1-Diphenylethylene Glycol (7).**—A 500-mg. sample of 1,1-diphenylethylene glycol[9] (m.p. 121.0–121.5°) was subjected to the same experimental conditions used above for effecting the solvolysis of 1 at pH 11.3. Unchanged glycol (498 mg.), m.p. 121.0–121.5°, was recovered; its infrared spectrum was completely devoid of carbonyl absorption. Thus, the glycol cannot be the source of the diphenylacetaldehyde and benzophenone encountered in the solvolyses of the halohydrins and epoxide **6** in the presence of base.

Similarly, when deoxybenzoin, benzhydrol, 1,1-diphenylethanol,[25] 1,1-diphenyl-2-fluoroethylene (**2**), and 1,1-diphenyl-2,2-difluoroethanol[26] were subjected to the same experimental conditions used with glycol **7**, no reaction occurred; each compound was recovered intact in high yield.

Oxidative Cleavage of Diphenylacetaldehyde to Benzophenone. A. By Heating in Dioxane–Water–Sodium Carbonate.—To a solution of 1.00 g. of diphenylacetaldehyde,[27] found by quantitative infrared analysis (CCl_4) to be contaminated with 6% of benzophenone, in 30 ml. of dioxane was added a solution of 600 mg. of sodium carbonate in 30 ml. of water. The resulting mixture, which became homogeneous on warming, was heated under reflux for 24 hr. and then allowed to stand an additional 24 hr. at room temperature. The light yellow reaction mixture was extracted twice with 100-ml. portions of ether and the combined ether extracts were washed three times with 60-ml. portions of water and dried. Removal of the ether on the steam bath followed by further concentration of the product *in vacuo* at 85–90° yielded a yellow oil, which weighed 940 mg. Quantitative infrared analysis of a 100-mg. aliquot of this oil showed 38% of benzophenone was present.

B. **By Aerial Oxidation.**—A 67-mg. sample of diphenylacetaldehyde,[27] free of benzophenone, was spread over an area of *ca.* 1 cm.^{2} on a glass slide and allowed to stand exposed to the atmosphere for 2 months while protected from dust. At the end of this time, the oily film on the slide had turned light yellow and weighed 55 mg. Quantitative infrared analysis (CCl_4 solution) showed that this material contained 37% of benzophenone and 41% of diphenylacetaldehyde. The rest of the material appeared to be polymeric in nature and was not identified.

Thermal Isomerization of 1,1-Diphenylethylene Oxide (6). A. In Dioxane as Solvent.—Spectroquality dioxane[21] was heated under reflux for 24 hr. over sodium metal to remove traces of water. A 100-mg. quantity of 1,1-diphenylethylene oxide was dissolved in 3.0 ml. of this solvent and the resulting solution was heated at reflux for 24 hr. and then cooled to room temperature. Removal of the solvent at reduced pressure at 75–85° gave a colorless oil which weighed 96 mg. Quantitative infrared analysis (CCl_4 solution) by the method described above showed that this material consisted of unchanged epoxide, 38% of diphenylacetaldehyde, and 9% of benzophenone. The absence in the spectrum of absorption bands in the region of the O–H stretching vibrations established that no 1,1-diphenylethylene glycol was present in the mixture.

The thermal rearrangement of **6** in dry benzene was carried out according to the foregoing procedure; the results are summarized in Table II.

B. **Neat.**—In a typical experiment a 100-mg. quantity of 1,1-diphenylethylene oxide was heated for 2.5 hr. at 200° in an atmosphere of dry nitrogen. The resultant amber oil weighed 98 mg. and was shown by quantitative infrared analysis (CCl_4 solution) to consist of 97% of diphenylacetaldehyde and approximately 3% of benzophenone. The crude oil had n^{25}D 1.5935 (lit.,[27] for diphenylacetaldehyde, n^{25}D 1.5875–1.5877) and was further characterized by conversion to its 2,4-dinitrophenylhydrazone, m.p. 151–152°, not depressed when mixed with an authentic sample[23] of diphenylacetaldehyde 2,4-dinitrophenylhydrazone.

The results of related thermal experiments are summarized in Table II.

Reaction of Phenylmagnesium Bromide with Phenacyl Fluoride.—Following the procedure of Bergmann and Kalmus,[14] the reaction at reflux temperature of 33 mmoles of phenylmagnesium bromide, prepared from bromobenzene (5.35 g.), magnesium (0.80 g.), and ether (25 ml.), with a solution of 4.60 g. (33 mmoles) of phenacyl fluoride in 10 ml. of ether, yielded 7.20 g. of an orange-colored oil. One-half of this oil was dissolved in 200 ml. of hexane and the resulting solution was applied to a column (50 cm. × 2.0 cm. diameter) of neutral alumina. Five main fractions (1–5, in the order of appearance) were isolated when the material was eluted successively with hexane, hexane–benzene, and benzene–ethanol mixtures.

Fraction 1 was biphenyl, 228 mg., m.p. 65–69° (lit.[28] m.p. 70°), whose identity was established by a mixture melting point determination and by infrared analysis.

Fraction 2 was triphenylethylene, 118 mg., m.p. 66–67° (lit.[17] m.p. 62°), identical in all respects with an authentic sample. This compound was probably formed during the chromatographic separation from a small amount of 1,1,2-triphenylethanol (**10**) produced during the course of the reaction. This olefin was not detected when the same chromatographic procedure was used to analyze the crude reaction product, rich in the isomeric secondary carbinol (**9**), obtained from the action of phenylmagnesium bromide on 1,1-diphenylethylene oxide (*vide infra*).

Fraction 3 was deoxybenzoin, 1.23 g. (38% yield based on phenacyl fluoride), m.p. 52–55° (lit.[29] m.p. 60°), identified by a mixture melting point, by infrared analysis, and by conversion to the 2,4-dinitrophenylhydrazone, m.p. 200.0–201.5° (lit.[29] m.p. 204°).

Fraction 4 was 1,2,2-triphenylethanol (**9**), 296 mg. (13% yield based on Grignard reagent), m.p. 87–88°, identical in all respects with an authentic sample, whose preparation is described below. The acetate had m.p. 156–157° (from ethanol) (lit.[15] m.p. 158°), not depressed on admixture with an authentic specimen.

Fraction 5 was a yellow, viscous oil, 976 mg., which was intractable. A sizable portion of the chromatographic column was colored yellow at the completion of the elution.

Formation of 1,2,2-Triphenylethanol (9). A. From Phenylmagnesium Bromide and 1,1-Diphenylethylene Oxide (6).—This reaction was carried out in an atmosphere of dry nitrogen. The stirred Grignard reagent, prepared from 0.50 g. (0.0205 g.-atom) of magnesium turnings and 3.20 g. (20.4 mmoles) of bromobenzene in 20 ml. of ether, was cooled to room temperature and treated with a solution of 4.00 g. (20.4 mmoles) of 1,1-diphenylethylene oxide[4] in 10 ml. of ether. The addition of epoxide required 15 min. and was accompanied by a mildly exothermic reaction. The resulting mixture was heated under reflux for 45 min. and then allowed to stand at room temperature overnight. The stirred reaction mixture was cooled in an ice bath and decomposed by slowly adding 20 ml. of a cold, saturated solution of ammonium chloride in water. The ether layer was separated and the aqueous phase was extracted three times with 15-ml. portions of ether. The combined ether extracts were washed twice with 20-ml. portions of water and dried. Removal of the ether on the steam bath afforded 5.63 g. of a light yellow oil which crystallized when cooled. Infrared analysis (CCl_4 solution) and thin layer chromatography (19:3 mixture of hexane–ethyl acetate developer) of this crude product showed that it was composed mainly of 1,2,2-triphenylethanol, contaminated with small amounts (*ca.* 15% total) of diphenylacetaldehyde, benzophenone, and biphenyl. Column chromatography of a portion of the reaction mixture on neutral alumina using in succession hexane and hexane–benzene and benzene–ethanol mixtures as eluents did not reveal the presence of any other compounds. Two recrystallizations of a 2.00-g. sample of the reaction product from ligroin (b.p. 66–75°) yielded 1.20 g. (corresponding to an over-all yield of 60%) of **9**, m.p. 87–88°, not depressed on admixture with a genuine sample prepared from diphenylacetaldehyde and phenylmagnesium bromide by the procedure described below. Further proof of the identity of **9**

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[25] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.

[26] J. Bornstein, M. S. Blum, and J. J. Pratt, Jr., *J. Org. Chem.*, **22**, 1210 (1957).

[27] D. J. Reif and H. O. House, *Org. Syn.*, **38**, 26 (1958).

[28] See ref. 24, p. 504.

[29] See ref. 24, p. 365.

was obtained by infrared spectral comparison with the authentic specimen and by its conversion to the corresponding acetate, which had m.p. 156–157° (lit.[15] m.p. 158°) and was identical in all respects with an authentic specimen.

B. **From Phenylmagnesium Bromide and Diphenylacetaldehyde.**[30]—To a stirred Grignard solution, prepared from 0.70 g. (0.029-g.-atom) of magnesium turnings, 5.00 g. (32.0 mmoles) of bromobenzene, and 10 ml. of ether, was added in a nitrogen atmosphere and at room temperature during the course of 15 min. a solution of 5.00 g. (25.5 mmoles) of diphenylacetaldehyde[27] in 15 ml. of ether. The resulting mixture was heated under reflux for 1 hr. and then cooled in an ice bath while 20 ml. of a saturated solution of ammonium chloride in ice–water was added slowly with stirring. The ether layer was removed and the aqueous phase was extracted twice with 50-ml. portions of ether. The combined ethereal extracts were washed twice with 30-ml. portions of water, dried, and concentrated under reduced pressure to give 6.84 g. of a solid residue. Two recrystallizations of the solid residue from ligroin (b.p. 66–75°) afforded 4.5 g. (64%) of 1,2,2-triphenylethanol (9), m.p. 87–88° (lit.[15] m.p. 86–87°). The corresponding acetate, isolated as colorless needles from a 1:1 mixture of benzene–ligroin, had m.p. 155.5–156.0° (lit.[15] m.p. 158°).

It was of interest to determine the mixture melting point of **9** and its isomer **10** since both carbinols have practically the same melting point. A genuine specimen of **10**, prepared from the reaction of phenylmagnesium bromide with deoxybenzoin according to the method of Klages and Heilmann,[17] had m.p. 88–89° (from ligroin), depressed to 83.5–89.0° when mixed with an equal weight of **9**. The infrared spectra in CCl_4 solution of the two carbinols are readily distinguishable.

Reaction of Phenyllithium with 1,1-Diphenylethylene Oxide (6). Formation of 1,1,2-Triphenylethanol (10) and 1,2,2-Triphenylethanol (9).—The reaction in an atmosphere of dry nitrogen of 0.019 mole of ethereal phenyllithium with 4.32 g. (0.022 mole) of 1,1-diphenylethylene oxide was carried out at reflux temperature for 2 hr. as described by Cristol, Douglass, and Meek.[4] The crude reaction product was a straw-colored oil which weighed 4.83 g. Its infrared spectrum (CCl_4 solution) displayed strong absorption in the hydroxyl region at 2.73 μ and revealed the presence of 8% diphenylacetaldehyde, *ca.* 1% benzophenone, and some unchanged epoxide. The identities of the carbonyl-containing components were established by gas chromatography using authentic samples of these compounds for comparison of retention times. Thin layer chromatography (4:1 mixture of hexane-ethyl acetate developer) showed that the crude reaction product contained a large amount of 1,1,2-triphenylethanol (10) and a relatively smaller amount of the isomeric carbinol, 1,2,2-triphenylethanol (9). Chromatography of a 2.00-g. portion of the oil on a silica gel column (43 cm. × 2.0 cm. diameter) using successively hexane and mixtures of hexane-ethyl acetate of increasing polarity as eluents and thin layer chromatography to monitor the fractions collected, gave five fractions (1–5, in order of appearance).

Biphenyl (1), 83 mg., m.p. 65–68° (lit.[28] m.p. 70°), was identified by a mixture melting point and by infrared spectral comparison with an authentic sample.

Fraction 2 was identified as triphenylethylene, 202 mg., m.p. 64–67° (lit.[17] m.p. 62°); the infrared spectrum of this material was exactly like that of an authentic sample of the ethylene.

The infrared spectrum of fraction 3, 356 mg. of an oil, indicated that it was mainly a mixture of diphenylacetaldehyde and benzophenone.

Fraction 4, identified as 1,1,2-triphenylethanol (10), 1.02 g. (47%), m.p. 86–88° (lit.[17] m.p. 88°), melted at 88–89° after one recrystallization from ligroin (b.p. 66–75°). Its infrared spectrum (CCl_4 solution) was indistinguishable from the spectrum of an authentic sample.[17]

Fraction 5, identified as 1,2,2-triphenylethanol (9), 52 mg. (2.4%), had m.p. 86.5–87.0° (lit.[15] m.p. 86°) after one recrystallization from a 1:1 mixture of benzene–hexane. The mixture melting point with an authentic sample, whose preparation is described above, was unchanged; both samples had identical infrared spectra in CCl_4 solution.

Carbinol **9** could be isolated more conveniently and in higher yield as its acetate. Thus, heating of the crude reaction mixture (1.70 g.) under reflux for 45 min. with 5 ml. of acetic anhydride gave a straw-colored solution which was poured onto a mixture of ice (15 g.) and water (15 ml.). After the excess anhydride had been hydrolyzed, the resulting oily suspension was extracted twice with 50-ml. portions of ether and the combined ether extracts were washed successively with water (two 50-ml. portions). Concentration of the dried solution under reduced pressure gave an oil which was taken up in 7 ml. of a 1:1 mixture of benzene-hexane, seeded with an authentic sample of the acetate of **9**, and then refrigerated for 4 days. The colorless needles thus obtained weighed 130 mg. (6.2%) and had m.p. 150–155°, which was raised to 155.5-156.5° (lit.[15] m.p. 158°) after one recrystallization from the same solvent mixture. This compound was shown by a mixture melting point determination and infrared spectral comparison to be identical with the acetate derived from the carbinol prepared above by the addition of phenylmagnesium bromide to diphenylacetaldehyde.

The reaction of phenyllithium with 1,1-diphenylethylene oxide was also carried out at room temperature for 24 hr.; the results of this experiment were essentially the same as those realized when the reaction was carried out at reflux temperature for 2 hr.

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[30] We are indebted to Mr. F. X. Doyle, S.J., for carrying out this reaction.

Organoboron Compounds. XX. Chemistry of Some 1-Naphthaleneboronic Acids with Substituents in the 8-Position[1]

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The preparation and some properties of naphthalene compounds with a borono group in the 1-position and a benzimidazolyl, borono, or carboxyl group in the 8-position are described.

The 1,8-disubstituted naphthalene compounds have provided a convenient system for investigating reactions of functional groups held close together in a fixed spatial relationship.[4] In the present paper we report the synthesis and characterization of naphthalene compounds which possess a borono group in the 1-position and a benzimidazolyl, borono, or carboxyl group in the 8-position. Unusual chemical properties resulting from the juxtaposition of the functional groups are noted.

Compound I.—The synthesis of 2-(8-borono-1-naphthyl)benzimidazole (I) was patterned after the procedure used for preparing 2-(2-boronophenyl)benzimida-

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[1] This research was supported by the Materials Research Center of Northwestern University and by the National Science Foundation. Paper XIX: R. L. Letsinger, "Brown-Nitrogen Chemistry," Advances in Chemistry Series 42, American Chemical Society, Washington, D. C., 1964, p. 1. Paper XVIII: J. D. Morrison and R. L. Letsinger, *J. Org. Chem.*, **49**, 3405 (1964).

[2] Dow Chemical Co. Fellow, 1961-1962.

[3] National Science Foundation Fellow, 1958-1959.

[4] R. L. Letsinger and J. A. Gilpin, *J. Org. Chem.*, **49**, 243 (1964), and earlier papers in the series on *peri*-substituted naphthalene compounds.