nol). *Anal.* Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.39; H, 8.71.

(±)-**2-Phenyl-1-pentanol (XII).**—In a procedure similar to the reduction of (±)-VI, 1.9 g. (0.01 mole) of (±)-XI, b.p. 123–125° (17 mm.), prepared from (±)-X,[29] was reduced with 0.3 g. (0.008 mole) of lithium aluminum hydride to give 1.5 g. (94%) of (±)-XII, colorless oil, b.p. 130–135° (17 mm.). *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.21; H, 9.75.

(−)-**2-Phenyl-1-pentanol (XII).**—A similar reduction of 0.7 g. of (−)-XI, b.p. 123–125° (17 mm.), $[\alpha]$D −72° (*c* 2.11 in methanol), prepared from (−)-X, $[\alpha]$D −68° (*c* 1.26 in benzene, 85% optical purity), which was obtained by resolution of the (+)-α-phenylethylamine salt,[7,9] gave 0.6 g. (98%) of (−)-XII, b.p. 130–133° (17 mm.), $[\alpha]$D −12° (*c* 3.76 in methanol). *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.28; H, 9.61.

Tosylation. (±)-**1,5-Ditosyl-2-phenylpentanediol (VIII).**—To a solution of 2 g. (0.011 mole) of (±)-VII in 12 ml. of dry pyridine was added 4.5 g. (0.024 mole) of *p*-tosyl chloride at 0°. After standing overnight, the mixture was poured onto ice, and recrystallization of the precipitated material from methanol gave 3.2 g. (65%) of colorless needles, m.p. 89–90.5°. *Anal.* Calcd. for $C_{25}H_{28}S_2O_6$: C, 61.45; H, 5.77. Found: C, 61.31; H, 5.53.

(+)-**1,5-Ditosyl-2-phenylpentanediol (VIII).**—Compound (+)-VIII, similarly prepared from 1.3 g. of (+)-VII, was obtained in 1.6 g. (46%) of colorless long needles, m.p. 66–67°, $[\alpha]$D +10° (*c* 2.92 in acetone), which seems to be pure enantiomer. *Anal.* Calcd. for $C_{25}H_{28}S_2O_6$: C, 61.45; H, 5.77. Found: C, 61.37; H, 5.60.

(±)-**1-Tosyl-2-phenylpentanol (XIII).**—In a procedure similar to that used for preparation of (±)-VIII, 2 g. of (±)-XIII, colorless needles, m.p. 68.5–69.5°, was obtained from 1.2 g. of (±)-XII; yield 86%. *Anal.* Calcd. for $C_{18}H_{22}SO_3$: C, 67.89; H, 6.96. Found: C, 67.72; H, 7.25.

(−)-**1-Tosyl-2-phenylpentanol (XIII).**—Compound (−)-XIII (0.9 g.), colorless rods, m.p. 42–43.5°, $[\alpha]$D −8.0° (*c* 8.50 in acetone), was similarly prepared in 71% yield from 0.65 g. of (−)-XII. *Anal.* Calcd. for $C_{18}H_{22}SO_3$: C, 67.89; H, 6.96. Found: C, 68.08; H, 6.99.

Reduction of Tosylates to 2-Phenylpentane (IX).[30] **Reduction of** (±)-**VIII.**—To a solution of 1.7 g. (0.045 mole) of lithium aluminum hydride in 40 ml. of dry ether was dropped with stirring at room temperature a solution of 2.8 g. (0.056 mole) of (±)-VIII in 20 ml. of tetrahydrofuran. The mixture was refluxed under stirring for two hours. After cooling, excess hydride was decomposed carefully with water, and the hydroxides were dissolved in dilute hydrochloric acid. The ethereal layer was separated, washed with 2 *N* sodium carbonate solution and water, dried over anhydrous sodium sulfate and concentrated. Distillation of the residue gave colorless mobile liquid (0.8 g.), b.p. 188–190°. The accompanying unsaturated hydrocarbon was removed by formation of the adduct with 2,4-dinitrobenzenesulfenyl chloride according to Cram.[23] The product free from unsaturated hydrocarbon was distilled twice over a few pieces of metallic sodium to give 0.4 g. (47%) of pure (±)-IX, b.p. 190–193° (lit.[23] 191–193°). The infrared spectrum showed good agreement with that reported by Cram.[23] This hydrocarbon (0.2 g.) was acetylated with acetyl chloride (0.2 g.) in carbon disulfide (5 ml.) in the presence of anhydrous aluminum chloride (0.3 g.) to yield 4-(2′-pentyl)-acetophenone (XIV) (0.15 g.), b.p. 142–147° (21 mm.). The semicarbazone, prepared by the usual procedure, was recrystallized from dilute ethanol in colorless needles, m.p. 175–176.5° (lit.[23] 175–177°). *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 67.96; H, 8.46.

Reduction of (+)-**VIII.**—Compound (+)-IX, obtained in 35% yield from (+)-VIII, had b.p. 190–193° (lit.[23] 191–193°), $[\alpha]$D +16° (*c* 1.52 in *n*-hexane) (lit.[23] αD +15.0° homogeneous) and an infrared spectrum identical with that of the racemic form. The corresponding acetophenone semicarbazone had m.p. 170–173.5°. *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 67.97; H, 8.53.

Reduction of (±)-**XIII.**—In a procedure similar to the reduction of (±)-VIII, reduction of 1.6 g. (0.005 mole) of (±)-XIII with 0.5 g. (0.013 mole) of lithium aluminum hydride in 35 ml. of dry ether and purification with 2,4-dinitrobenzenesulfenyl chloride gave 0.3 g. (50%) of colorless mobile liquid, b.p. 190–193°. The infrared spectrum showed complete correspondence with that of (±)-IX prepared from (±)-VIII and also with that reported by Cram.[23] The corresponding acetophenone semicarbazone was similarly prepared, m.p. 174.5–176°, and showed no depression in melting point when mixed with that prepared from (±)-VIII. *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 67.99; H, 8.40.

Reduction of (−)-**XIII.**—Similar treatment starting with 0.9 g. of (−)-XIII gave 0.2 g. (48%) of (−)-IX, b.p. 191–193°, $[\alpha]$D −16.5° (*c* 1.42 in *n*-hexane). Its infrared spectrum was identical with that of the racemic form. The corresponding acetophenone semicarbazone had m.p. 169–173°. *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 68.02; H, 8.61.

Acknowledgment.—The authors wish to express their sincere thanks to Prof. Sankichi Takei for his constant encouragement, and to Prof. Karl Freudenberg for his suggestive discussions at the Annual Meeting of the Agricultural Chemical Society of Japan, May, 1958. They are also grateful to the Ministry of Education, Japanese Government, for a grant in aid.

KYOTO, JAPAN

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[29] A. Rossolymo, *Ber.*, **22**, 1235 (1889).

[30] The authors are indebted to Laboratory of Agricultural Chemicals, Kyoto University, for the infrared spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

peri-Substituted Naphthalenes. I. New Rearrangement Reactions of Substituted Naphthopyrans

BY ROBERT L. LETSINGER AND PETER T. LANSBURY[1]

RECEIVED AUGUST 4, 1958

Two new rearrangement reactions were observed in the course of investigating the effect of acids on substituted 1,8-naphthalene compounds: (1) 1-hydroxy-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran (II) isomerized to 8-benzhydryl-1-naphthoic acid (VIII) (1,5-hydrogen shift), and (2) 1-methylene-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran (III) rearranged to 3,3-diphenyl-2,3-dihydro-1H-benzonaphthen-1-one (XI). In the presence of acid, 1,8-bis-(phenylhydroxymethyl)-naphthalene (I) dehydrated without rearrangement to give a cyclic ether (IV). The yields in all three reactions were close to quantitative.

The 1,8-disubstituted naphthalene system is particularly well suited for investigations of intramolecular interactions of functional groups. Firstly, the substituents are held firmly in close proximity. The facile conversion of 1,8-bis-bromomethylnaphthalene to acenaphthene by phenyllithium illustrates the ease of bonding across these positions.[2]

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[1] National Science Foundation Predoctoral Fellow, 1955–1956. Financial assistance for this work was also provided by the du Pont Co. and the Abbott Fund of Northwestern University.

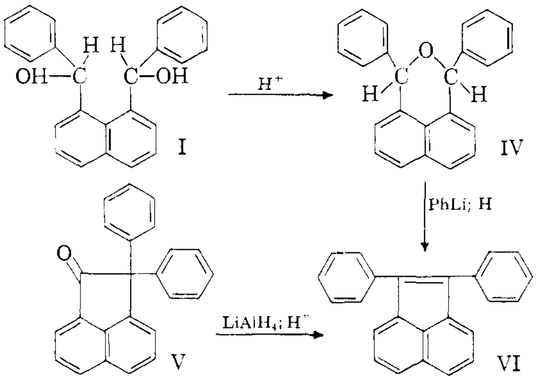
[2] E. Bergmann and J. Szmuszkovicz, THIS JOURNAL, **75**, 2760 (1953).

Secondly, electronic coupling of the 1,8-positions *via* the naphthalene nucleus seems to be small, as indicated by the orientation for electrophilic substitutions. Finally, a considerable number of compounds which may serve as starting reagents or reference substances are known and readily can be prepared.[3] In looking for new types of rearrangements and functional group interactions we have therefore studied a variety of 1,8-disubstituted naphthalene compounds. The effects of acidic solutions on 1,8-bis-(phenylhydroxymethyl)-naphthalene (I), 1-hydroxy-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran (II) and 1-methylene-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran (III) are considered in this paper.

Compounds I and II were prepared by reduction of 1,8-dibenzoylnaphthalene and 3,3-diphenyl-1,8-naphthalide with lithium aluminum hydride. Compound III was obtained by dehydration of the hemiketal formed by addition of methylmagnesium iodide to diphenylnaphthalide.

The reduction of 3,3-diphenyl-1,8-naphthalide was unusual in that the product was a hemiacetal (II), even though a large excess of reducing agent was employed. Cyclic hemiacetals have previously been isolated from reactions involving lithium aluminum hydride; however, they were susceptible to further reduction by the hydride.[4] The lack of carbonyl activity of II may be attributed to the presence of the *gem*-diphenyl group[5] and the rigidity of the *peri*-naphthopyran ring. In contrast, 1,8-dibenzoylnaphthalene was reduced by lithium aluminum hydride to the diol I in high yield (96%). Attempts to prepare a hemiketal by partial reduction were unsuccessful.[6]

Compound I.—It was of interest to see whether Compound I would dehydrate in acid solution like benzhydryl alcohol to give an ether, or whether it might dehydrate with phenyl migration like 1,2-diphenylacenaphthenediol,[3] which differs structurally from I in that the carbon substituents at the 1,8-positions of naphthalene are directly joined.



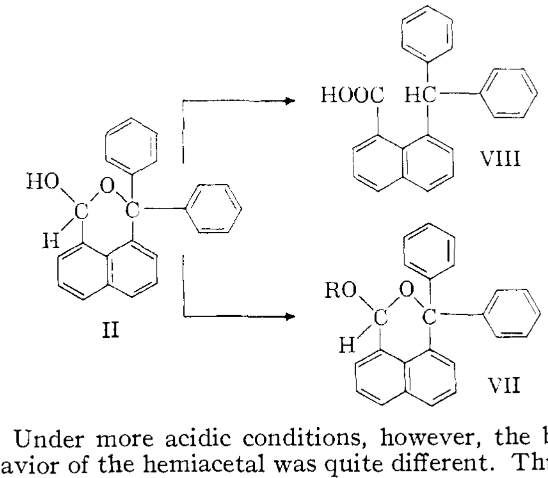
Compound I was heated for two days with a solution of formic acid containing toluenesulfonic acid. From this reaction was isolated a 92% yield of a dehydration product identified as the cyclic ether IV by analysis and the infrared spectrum. The carbonium ion generated at the 1-position therefore interacted with the nearby nucleophilic oxygen rather than with the phenyl group.

The action of phosphorus tribromide on I also led to formation of IV. A similar cyclization of 1,8-bis-hydroxymethylnaphthalene has been reported by Boekelheide and Vick.[7]

Wittig, Davis and Koenig[8] prepared phenanthrene by successive treatment of the cyclic oxide of 2,2′-bis-(hydroxymethyl)-biphenyl with phenyllithium and acid. An analogous reaction with IV should give 1,2-diphenylacenaphthylene (VI). In support of the structure assigned to IV, we obtained this orange colored hydrocarbon by treating IV with phenyllithium and then warming the reaction product with formic acid; VI was also prepared for comparison purposes by reducing ketone V with lithium aluminum hydride and dehydrating the resulting alcohol with formic acid. This latter sequence provides a convenient synthetic route to VI.

Compound II.—This hemiacetal was selected next for investigation since on acid treatment it could give rise to a carbonium ion (at carbon on the 1- or 8-position in naphthalene) which could not be satisfied by cyclic ether formation as in I. The possibility for an acid-catalyzed rearrangement therefore appeared good.

When II was heated in methyl or ethyl alcohol which contained a small amount of sulfuric acid, it formed the corresponding acetals (VIIa, R = CH_3; VIIb, R = C_2H_5) in good yield. This reaction shows that acid-catalyzed reactions may be carried out at the aldehydic carbon without a rearrangement ensuing.



Under more acidic conditions, however, the behavior of the hemiacetal was quite different. Thus, when heated for half an hour with formic acid or with acetic acid containing iodine or sulfuric acid, II was isomerized quantitatively to 8-benzhydryl-1-naphthoic acid (VIII). The ethyl acetal VIIb also afforded VIII under these conditions. The net effect is that of a dismutation in which carbon at

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[3] The syntheses of W. E. Bachmann and E. Chu, THIS JOURNAL, **58**, 1118 (1936), have been particularly useful.

[4] (a) F. Hochstein, *ibid.*, **71**, 305 (1949); (b) G. Arth, *ibid.*, **75**, 2413 (1953).

[5] T. A. Geissman and L. Morris, *ibid.*, **63**, 1111 (1941), have commented on the unusual stability of lactones bearing a *gem*-diphenyl group adjacent to the oxygen atom.

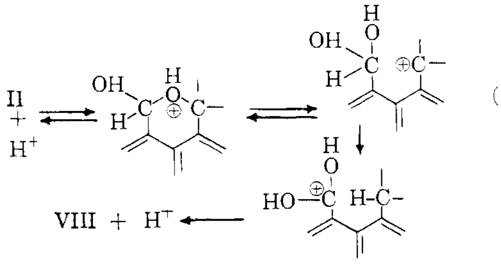
[6] It may be noted, however, that 1,8-dibenzoylnaphthalene reacts with phenyllithium to give the hemiketal rather than a glycol; G. Wittig, M. Leo and W. Wiener, *Ber.*, **64**, 2405 (1931).

[7] V. Boekelheide and G. Vick, THIS JOURNAL, **78**, 653 (1956).

[8] G. Wittig, P. Davis and G. Koenig, *Ber.*, **84**, 627 (1951).

the alcohol stage of oxidation is reduced to the hydrocarbon stage, while carbon at an aldehyde stage is oxidized to a carboxylic acid. To the best of our knowledge a dismutation of this type has not previously been observed, though hydride shifts in strong acid solutions are common. A related transformation is that of benzhydryl ether to diphenylmethane and benzophenone.[9]

A plausible path for this rearrangement is represented by sequence 1, according to which a hydride ion shifts intramolecularly to an adjacent triarylcarbonium ion. An alternate pathway involving an intermolecular hydride shift is much less plausible on steric grounds. Moreover, an intermediate in the intermolecular process would be ion IX, a protonated form of diphenylnaphthalide. It is highly unlikely that this ion is involved directly in the rearrangement just described because 3,3-diphenyl-1,8-naphthalide is very resistant to acid reduction. Not only boiling formic acid but also a refluxing mixture of hydriodic acid and phosphorus was without effect on this compound.



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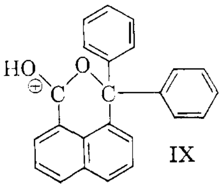
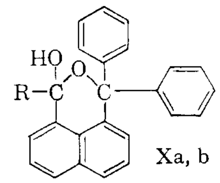


IX

Compound III.—In view of the rearrangement, II → VIII, an investigation of the effect of acid on Xa (R = CH_3) was deemed worthwhile. Should Xa react as II, it would provide an example of a 1,5-methyl shift. Although 1,2-methyl transfers are well known, analogous 1,3-, 1,4-, 1,5-, etc., shifts have not yet been demonstrated in spite of many experiments well designed for observation of such phenomena.[10]

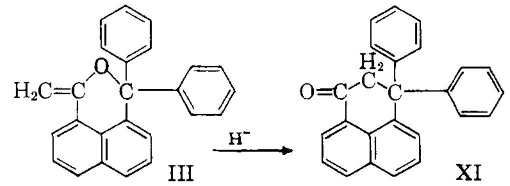
Geissman and Morris[5] prepared a series of hemiketals of type Xb in which R was ethyl, *n*-butyl, isopropyl and *sec*-butyl. They reported that these substances developed a yellow color in sulfuric acid, formed crystalline ferrichlorides when heated with hydrogen chloride and ferric chloride in acetic acid, and dehydrated to alkylidene derivatives when heated with acetic anhydride and sodium acetate; however, they did not observe any rearrangements.



Xa, b

On extending their synthetic procedure, which involved hydrolysis of a Grignard complex with dilute ammonium chloride, to the preparation of Xa, we obtained a mixture. The infrared spectrum indicated that it consisted of the expected tertiary alcohol Xa and its dehydration product III. From a similar reaction in which hydrolysis was accomplished with dilute sulfuric acid, a 71% yield of III was obtained. Its structure was deduced from the mode of preparation, the infrared spectrum and analytical data. Since III should be equivalent to Xa in acid solutions, further efforts to obtain pure Xa were abandoned.

Compound III gave a green color in an acetic–sulfuric acid solution. After the solution had been refluxed for 12 hours, however, the color was blood-red. Dilution with water then afforded in 94% yield a ketone isomeric with III; there was no evidence for formation of a carboxylic acid, which would have resulted if a methyl group had migrated. The presence of the carbonyl group was indicated by strong absorption at 5.9 mμ and by the preparation of a 2,4-dinitrophenylhydrazone. On the basis of these data and the nature of the reaction, structure XI was assigned to the new compound.



The vinyl ether III like hemiacetal II therefore isomerized smoothly in acid solution; however, the two rearrangements differ in type. Rearrangement III → XI involves isomerization of an enol ether to a ketone.[11] Generally enol ethers undergo polymerization or hydrolytic cleavage in the presence of acids. The rearrangement observed here may be attributed to the geometry of the system and the ease of forming a triarylmethylcarbonium ion. No doubt in the course of the reaction an enol is generated in the vicinity of a triarylmethyl carbonium ion. Addition of the carbonium ion to the enol and loss of a proton would complete the reaction.

Formula XII represents a conceivable, though improbable, structure for the product from III. The position of the carbonyl band in the infrared spectra should be about the same for XI and XII, and the carbon–hydrogen analytical data are not sufficiently precise to differentiate conclusively between these two formulas. In order to exclude

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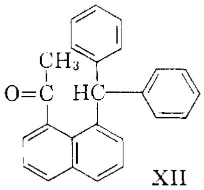
[9] (a) H. Burton and G. Cheesman, *J. Chem. Soc.*, 986 (1953); (b) G. Baddeley and W. Pickles, *ibid.*, 3726 (1953).

[10] (a) R. K. Maudgal, T. T. Tchen and K. Bloch, THIS JOURNAL, **80**, 2589 (1958); (b) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **80**, 630 (1958); (c) V. Prelog and W. Kung, *Helv. Chim. Acta*, **39**, 1394 (1956); (d) J. Meinwald, THIS JOURNAL, **77**, 1617 (1955).

[11] Isomerization of vinyl ethers to carbonyl compounds has been effected by pyrolysis; see, for example, R. L. Hasche and B. Thompson, U. S. Patent 2,294,402; *C. A.*, **37**, 891 (1943).

An acid-catalyzed reaction which bears some similarity to this one is the conversion of the enol acetate of ethyl acetoacetate to a mixture of ethyl diacetylacetate and ethyl acetoacetate (partial conversion of an enol acetate to a diketone) in the presence of boron trifluoride; see C. R. Hauser, F. C. Frostick and E. H. Man, THIS JOURNAL, **74**, 3232 (1952).

XII, we synthesized it independently by the reaction of methyllithium with methyl 8-benzhydryl-1-naphthoate. Although a great excess of methyllithium was employed an excellent yield (92%) of ketone XII was obtained. Evolution of gas in the course of the reaction indicated that a second mole of methyllithium enolized the ketone (with formation of methane), a general type of reaction of hindered alkyl ketones.[12] Compound XII was different from the product of rearrangement of III.



XII

It is interesting to note the relative ease of preparing carbonyl derivatives of V, XI and XII, which reflects the relative steric effects of the benzhydryl group in this series. The most reactive ketone was XI; it readily formed a 2,4-dinitrophenylhydrazone derivative under the usual conditions; V did not form a dinitrophenylhydrazone but did yield a hydrazone when suspended in refluxing hydrazine hydrate. Ketone XII was the least reactive, failing to react with either dinitrophenylhydrazine reagent or refluxing hydrazine hydrate.

Experimental Section

Melting points are uncorrected. Elemental analyses were performed by Miss Hilda Beck. All infrared spectra were taken with a Baird double beam spectrometer equipped with sodium chloride optics, using chloroform as solvent unless otherwise specified.

1,8-Dibenzoylnaphthalene, 2,2-diphenyl-1-acenaphthenone and 8-benzhydryl-1-naphthoic acid were prepared by the method of Bachmann and Chu[3]; 3,3-diphenyl-1,8-naphthalide was made by the procedure of Wittig, Leo and Wiener.[6]

1,8-Bis-(phenylhydroxymethyl)-naphthalene (I).—With the aid of a Soxhlet extractor, 2.10 g. (6.3 mmoles) of 1,8-dibenzoylnaphthalene was introduced slowly (20 hours) into a refluxing solution of 0.24 g. (6.3 mmoles) of lithium aluminum hydride in 150 ml. of ether. After hydrolysis of the reaction mixture with sodium carbonate solution, the ether layer was separated, evaporated, and mixed with petroleum ether (b.p. 60–70°). The crude product which separated, m.p. 195–196°, was recrystallized from 80% ethanol, yielding 2.00 g. (96%) of I, m.p. 199–200°. The infrared spectrum of I (taken in a potassium bromide plate) had strong bands at 3.0 and 9.9 μ and no absorption in the carbonyl region.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.62; H, 5.88.

The use of sodium borohydride in aqueous tetrahydrofuran for reduction of dibenzoylnaphthalene proved ineffective and resulted in the recovery of starting material.

1-Hydroxy-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran-(II).—A solution of 3.4 g. (10 mmoles) of 3,3-diphenyl-1,8-naphthalide in 100 ml. of dry tetrahydrofuran gradually was added (15 minutes) to a stirred solution of 1 g. (26 mmoles) of lithium aluminum hydride in 50 ml. of tetrahydrofuran. After the solution had refluxed for one hour, it was hydrolyzed with dilute sodium hydroxide solution and allowed to stand overnight. The precipitated inorganic material was removed by filtration and the filtrate evaporated to dryness, leaving a colorless oil which solidified on cooling. Recrystallization from petroleum ether gave 2.6 g. (76%) of II, m.p. 165.5–167°. The analytical sample melted at 166–167.5°; II was also preparable in 50% yield using ether as solvent and introducing the naphthalide *via* a Soxhlet extracter. The infrared spectrum showed bands at 2.73, 2.84 and 9.72 μ and no absorption in the 5.6–6.0 μ region. Compound II gave no derivative when refluxed for 15 minutes with 2,4-dinitrophenylhydrazine reagent.[13]

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.43; H, 5.23.

1-Methylene-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]-pyran (III).—3,3-Diphenyl-1,8-naphthalide (5.0 g., 15 mmoles) was added to a solution of methylmagnesium iodide (prepared from 1.2 g., 50 mmoles, of magnesium and 7.2 g., 50 mmoles of methyl iodide), in 150 ml. of ether. Stirring and refluxing were continued for 7 hours, whereupon the mixture was hydrolyzed with cold, dilute sulfuric acid. The ether layer was separated, dried with sodium sulfate, and partially evaporated. On treatment with petroleum ether, 3.5 g. (71%) of III precipitated, m.p. 220–223°. The analytical sample was obtained by two recrystallizations from dioxane–ethanol, m.p. 227.5–229°.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.79; H, 5.42. Found: C, 89.53; H, 5.17.

Compound III rapidly decolorized bromine in carbon tetrachloride and its infrared spectrum exhibited bands at 6.1 and 11.4 μ and no absorption in the hydroxyl or carbonyl regions.

In another experiment the hydrolysis of the Grignard complex was carried out with dilute ammonium chloride solution. The crude product (3.15 g. from 3.4 g. of diphenylnaphthalide) melted at 147–156°; after a recrystallization the melting point was 135–156°. Further recrystallization failed to decrease the melting range. The infrared spectrum contained bands attributable to both hydroxyl and vinyl groups.

Dehydration of I.—(a) A mixture of 0.50 g. of I, 0.40 g. of *p*-toluenesulfonic acid and 30 ml. of 90% formic acid was heated for two days on a steam-bath. The crystals which had formed were separated by filtration, washed with ethanol, and recrystallized from ethanol–acetone; yield 0.45 g. (92%), m.p. 201.5–202°. The infrared spectrum of IV exhibited strong bands at 9.4 and 9.7 μ (ether absorption) but no absorption in the hydroxyl region (2.6–3.0 μ).

Anal. Calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.62. Found: C, 90.12; H, 5.10.

(b) To a hot (70°) solution of phosphorus tribromide (0.87 g.) in 50 ml. of benzene containing a drop of pyridine was added 0.50 g. of IV. The temperature was maintained at 55° for two hours; then the solution was cooled, washed with 5% sodium bicarbonate solution and dried over sodium sulfate. Upon reduction of the volume by evaporation and addition of petroleum ether, 0.40 g. (85%) of IV, m.p. 200–202°, separated. Recrystallization of this material from chloroform–petroleum hexane sharpened the melting point to 202°. A mixture melting point with IV prepared by method (a) was undepressed and the infrared spectra of the two samples were identical.

Wittig Rearrangement of IV.—A solution of 0.20 g. of IV and 5.0 ml. of 0.94 *M* phenyllithium in 20 ml. of ether was refluxed overnight under nitrogen. Hydrolysis of the solution with dilute sulfuric acid gave an orange organic layer, which was washed and evaporated on a steam-bath. The residual orange oil was warmed for 15 minutes with formic acid containing a trace of *p*-toluenesulfonic acid. The solid which resulted was recrystallized from acetone, yielding 0.03 g. (16%) of 1,2-diphenylacenaphthylene, m.p. 156–159°, as orange needles. The melting point was not depressed when a sample of this material was mixed with diphenylacenaphthylene prepared as described in the next section.

Preparation of 1,2-Diphenylacenaphthylene from 2,2-Diphenyl-1-acenaphthenone. Step 1.—2,2-Diphenyl-1-acenaphthenone, m.p. 173–174°, was prepared in 93% yield from 1,2-diphenylacenaphthenediol by the method of Bachmann and Chu.[3] This ketone (3.0 g.) then was reduced with 0.23 g. of lithium aluminum hydride in 200 ml. of ether as described for the preparation of 1,8-bis-(phenyl-

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[12] Phenyllithium yields a tertiary carbinol on reaction with esters of 8-benzhydryl-1-naphthoic acid; G. Wittig and H. Petri, *Ber.*, **68**, 924 (1935). In this case enolization of the intermediately formed phenyl benzhydrylnaphthyl ketone is not possible.

[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

hydroxymethyl)-naphthalene. There was obtained 2.7 g. (90%) of a crystalline alcohol, m.p. 117.5–118.5°. Further recrystallization afforded a sample, m.p. 119.5°, which analyzed as a partial hydrate of 2,2-diphenyl-1-acenaphthenol. The infrared spectrum had a band at 2.8 μ and showed no absorption in the carbonyl region. An attempt to prepare a tosylate derivative was unsuccessful.

Anal. Calcd. for $C_{24}H_{18}O \cdot 1/3H_2O$: C, 87.77; H, 5.73. Found: C, 87.71; H, 5.64.

Step 2.—A sample (0.50 g.) of the alcohol thus prepared was warmed on a steam-bath with 15 ml. of 98% formic acid containing 0.20 g. of *p*-toluenesulfonic acid monohydrate. Initially the solution was colorless, but it soon became bright orange. After 15 minutes 15 ml. of water was added; on cooling, the orange hydrocarbon separated. Recrystallization from acetone yielded 0.42 g. (90%) of 1,2-diphenylacenaphthylene, m.p. 161.3°. The infrared spectrum was simple with sharp bands at 8.9, 9.28, 9.65, 9.8, 12.11 and 14.3 μ in addition to aromatic bands in the 5–7 μ region and carbon–hydrogen absorption at 3.28–3.32 μ.

1,2-Diphenylacenaphthylene also was obtained when 1.60 g. of 1,2-dichloro-1,2-diphenylacenaphthene,[3] m.p. 186–188°, in solution in 30 ml. of tetrahydrofuran was added to a slurry of 0.50 g. of lithium aluminum hydride in 50 ml. of tetrahydrofuran. The solution became orange-yellow, and after refluxing overnight was dark brown in color. Hydrolysis with water and separation of the crystalline product yielded 0.80 g. (62%) of crude diphenylacenaphthylene, m.p. 150–156°.

Preparation of VII, the Acetals of II.—The methyl acetal VIIa was prepared by refluxing 0.50 g. of II in 20 ml. of methanol containing two drops of sulfuric acid for 30 minutes. The white, crystalline acetal weighed 0.43 g. (83%) and melted at 183–184° (from methanol).

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 85.35; H, 5.69.

By a similar procedure the ethyl acetal VIIIb was obtained from 0.70 g. of II; yield 0.65 g. (86%), m.p. 197.5–198.5°. The infrared spectra of VIIa and b showed strong bands at 9.72 μ and no absorption at 2.6–3.0 μ.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.36; H, 6.02.

Rearrangement of II in Acid.—A solution of II (0.50 g.) and iodine (0.30 g.) in 25 ml. of glacial acetic acid was warmed for 30 minutes on a steam-bath, then poured into dilute sodium bisulfite solution. The precipitate was removed by filtration, washed with water, and dried. It weighed 0.50 g. (100%) and melted at 227–229°. Recrystallization from acetic acid raised the melting point to 231°. No melting point depression was observed when this product was mixed with an authentic sample of 8-benzhydryl-1-naphthoic acid.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.07; H, 5.27.

This isomerization was also carried out in better than 90% isolated yield by using as solvent (a) glacial acetic acid containing a drop of sulfuric acid or (b) formic acid. The product, obtained directly as white crystals by dilution with water, was essentially pure (m.p. 227–228°).

The ethyl acetal VIIb in acetic acid with a trace of sulfuric acid likewise yielded 8-benzhydryl-1-naphthoic acid (92% yield).

Stability of 3,3-Diphenyl-1,8-naphthalide in Acid.—To test the stability of IX in formic acid in the presence of an aromatic aldehyde (simulated conditions for an intermolecular rearrangement of II) 0.50 g. of 3,3-diphenyl-1,8-naphthalide (m.p. 205–206°) was warmed for 24 hours with a solution of 10 ml. of formic acid and 1.0 ml. of benzaldehyde. On cooling, filtering, and washing the crystals thus obtained with ethanol, we recovered 0.46 g. (92%) of the lactone, m.p. 205–206° (not depressed on mixture with an authentic sample).

The resistance of this naphthalide to acid reduction was demonstrated also by heating a sample of the naphthalide with constant boiling hydriodic acid and red phosphorus for a period of 24 hours, conditions which readily reduced not only triphenylcarbinol but also benzhydrol. 3,3-Diphenyl-1,8-naphthalide was recovered unchanged from this treatment.

Rearrangement of III in Acid.—A solution of 0.80 g. of III in 30 ml. of acetic acid, 4 ml. of water and 0.4 ml. of sulfuric acid was refluxed for 16 hours. The solution rapidly became dark green in color and then slowly acquired a reddish hue. By the end of the reflux period the color was crimson. The solution then was poured into three volumes of ice-water and the solids taken up in ether. The ether solution was washed with 5% sodium hydroxide (acidification of the alkaline extract yielded no organic acids) and dried over sodium sulfate. Evaporation of the ether left 0.75 g. (94%) of a tan solid, m.p. 196–197.5°. Several recrystallizations from ethanol–acetone (with charcoal treatment) yielded XI as creamy white crystals, m.p. 200.5–201°. The infrared spectrum had a strong band at 5.9 μ, and no absorption in the ether or double bond region. The absence of a double bond was indicated also by lack of reactivity with bromine in carbon tetrachloride.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.79; H, 5.42. Found: C, 89.40; H, 5.24.

A 2,4-dinitrophenylhydrazone derivative, prepared by standard techniques,[13] yielded bright scarlet needles, m.p. 269–271° dec.

Anal. Calcd. for $C_{31}H_{22}O_4N_4$: N, 10.87. Found: N, 11.06.

Preparation of Methyl 8-Benzhydryl-1-naphthyl Ketone (XII).—Methyl 8-benzhydryl-1-naphthoate[14] (1.10 g., 3.1 mmoles, m.p. 167–167.5°) was added to a solution of methyllithium which had been prepared from 0.76 g. of lithium and 14.2 g. of methyl iodide in 50 ml. of ether. Addition of the ester resulted in a rapid reaction during which a quantity of gas was evolved. After the yellow solution had refluxed for 5 hours, it was hydrolyzed with ice-water. The organic matter was extracted with ether. Concentration of the ether solution, after washing with water and drying as usual, and trituration of the residue with petroleum hexane yielded 0.96 g. (92%) of a white crystalline solid, which after recrystallization from ethanol melted at 164–165°. The infrared spectrum showed a strong carbonyl band at 5.9 μ, but otherwise was different from the spectrum of XI.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.12; H, 5.74.

This ketone did not form a 2,4-dinitrophenylhydrazine derivative and was recovered unchanged after treatment with refluxing 100% hydrazine hydrate for two hours.

Hydrazone of 2,2-Diphenylacenaphthenone.—A suspension of 1.0 g. of this ketone in 15 ml. of 100% hydrazine hydrate was refluxed for two hours. Upon cooling, crystals separated out. They were removed by filtration, washed with ethanol, and recrystallized from ethanol–acetone, yielding 1.0 g. (97%) of the hydrazone, m.p. 216–217°. The analytical sample, obtained after several more recrystallizations, melted at 217–218°.

Anal. Calcd. for $C_{24}H_{18}N_2$: N, 8.37. Found: N, 8.57.

An attempt was made to decompose this hydrazone by alkali to form 2,2-diphenylacenaphthene. A sample of the hydrazone (0.70 g.) was heated at 180–200° with 1.0 g. of potassium hydroxide in 15 ml. of ethylene glycol. On cooling and acidifying the solution with hydrochloric acid, a solid separated. Recrystallization of this material from acetone–ethanol gave 0.65 g. (93%) of 8-benzhydryl-1-naphthoic acid, m.p. 233°. The hydrazone, therefore, underwent cleavage analogously to the ketone, 2,2-diphenylacenaphthenone,[3] rather than a decomposition characteristic of the Wolff–Kishner reduction.

EVANSTON, ILL.

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[14] G. Wittig and H. Petri, *Ber.*, **68**, 924 (1935).