TABLE VII

ACID-CATALYZED CLEAVAGE OF ACYLARYLSULFINYLACETIC ACIDS

Acylarylsulfinylacetic acid	Thiol	Yield, %	B.p. (mm.), °C.
4-CH_3CO-2-$CH_3C_6H_3SOCH_2CO_2H$	4-CH_3CO-2-$CH_3C_6H_3SH$	43	143–144 (5)
2-CH_3CO-4-$CH_3C_6H_3SOCH_2CO_2H$	2-CH_3CO-4-$CH_3C_6H_3SH$[a]	45	139–140 (5.5)
4-C_6H_5CO-3-$CH_3C_6H_3SOCH_2CO_2H$	4-C_6H_5CO-3-$CH_3C_6H_3SH$[b]	39	152 (2)

[a] M.p. 32–33°. *Anal.* Calcd. for $C_9H_{10}OS$: C, 65.02; H, 6.06; S, 19.29. Found: C, 65.20; H, 6.19; S, 19.01. Disulfide, m.p. 178° (aqueous methanol). *Anal.* Calcd. for $C_{18}H_{18}O_2S_2$: C, 65.42; H. 5.49; S, 19.40. Found: C, 65.84; H, 5.47; S, 19.01. [b] *Anal.* Calcd. for $C_{14}H_{12}OS$: C, 73.65; H, 5.3; S, 14.04. Found: C, 74.15; H, 5.69; S, 13.24. S-Benzoyl derivative, m.p. 97.5–98.5 (methanol). *Anal.* Calcd. for $C_{21}H_{16}O_2S$: C, 76.18; H, 4.85; S, 9.64. Found: C, 76.72; H, 4.95; S, 9.68.

Anal. Calcd. for $C_9H_{10}O_3S$: C, 54.53; H, 5.08; S, 16.17. Found: C, 54.32; H, 4.91; S, 15.95.

This material gave no depression of melting point with an authentic sample prepared from 4-acetylphenylmethyl sulfide[14] by hydrogen peroxide oxidation.[15]

Thiols from Di(acylaryl) Disulfides.—The disulfide (0.05 mole) was refluxed in acetic acid (1 mole) and water (2 moles) and the mixture treated, over a period of 40 min., with zinc dust (0.3 to 0.4 mole). After refluxing for an additional 3 hr. the mixture was poured into water. Excess zinc was removed by adding a little concentrated hydrochloric acid. The oil was taken up in ether and crude thiol extracted from this with aqueous sodium hydroxide. Acidification of the sodium hydroxide solution gave crude thiol which was redissolved in ether; the ether was washed with water and dried. The ether was distilled and the thiol purified by vacuum distillation.

The reduction of di(4-benzoyl-3-methylphenyl) disulfide using zinc and acetic acid gave 4-benzyl-3-methylbenzenethiol as the major product. Table V summarizes the results obtained.

Acylarylthiols from Acylarylsulfinylacetic Acids. A. Preparation of Acylarylsulfinylacetic Acids.—Acylarylmercaptoacetic acid (0.1 mole) was suspended in 75% acetic acid (250 ml.) and the mixture stirred and heated to about 60°. Hydrogen peroxide (0.1 mole as a 30% aqueous solution) was added over 50 min. at this temperature. The mixture was kept at 60° for 5 hr. and allowed to stand overnight. Half of the solvent mixture was removed under vacuum at 50–60° (rotary evaporator). Cooling of the acetic acid solution sometimes led to crystallization of the acylarylsulfinylacetic acid. In a few cases the acylarylsulfinyl acetic acid was obtained as a sirup by complete evaporation of the aqueous acetic acid. Table VI summarizes the results obtained.

B. Cleavage of Acylarylsulfinylacetic Acids.—Acylarylsulfinylacetic acid (0.05 mole) was refluxed in 6% sulfuric acid (200 ml.) for 5 to 6 hr. The oily suspension was extracted with ether and the ether extracted first with aqueous sodium bicarbonate and then with aqueous sodium hydroxide. Acidification of the sodium bicarbonate extracts usually gave some acidic material (2-acetyl-4-methylphenylsulfinylacetic acid gave some high melting acid, probably 3,5-dimethylbenzo[*b*]thiophene-2-carboxylic acid or its sulfoxide). Acidification of the sodium hydroxide extracts gave the crude thiols which were purified by distillation. The neutral ether layer on evaporation usually yielded a small quantity of the disulfide (the neutral product from 2-acetyl-4-methylphenylsulfinylacetic acid was complex). Table VII summarizes the results obtained.

Hydrogen Peroxide Oxidation of 4-Nitrophenylmercaptoacetic Acid.—4-Nitrophenylmercaptoacetic acid (0.05 mole) was finely ground and suspended in water (55 ml.) containing 80% phosphoric acid (3 ml.). The suspension was boiled and hydrogen peroxide (0.055 mole as a 30% aqueous solution) added over about 30 min. Steam was passed in during the peroxide addition and for 1 hr. after that. The solid in the reaction flask turned first to a yellow oil and finally to a solid. About 0.5 g. of product steam distilled; this proved to be a mixture of about equal weights of 4-nitrobenzenethiol, m.p. 76–77°, and di(4-nitrophenyl) disulfide, m.p. 179–180°. The contents of the reaction flask were filtered and the solid extracted with aqueous sodium bicarbonate. Acidification of this extract gave 3 9 g. of acidic material, m.p. 155–160°. Several crystallizations of the latter from methanol afforded 4-nitrophenylsulfonylacetic acid, m.p. 168° dec.

Anal. Calcd. for $C_8H_7NO_6S$: N, 5.71; S, 13.06. Found: N, 5.76; S, 13.40.

The solid insoluble in aqueous sodium bicarbonate was di(4-nitrophenyl) disulfide, m.p. 175–177°. Crystallization from acetic acid gave a pure product, m.p. 180–181°

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[14] G. B. Bachman and C. L. Carlson, *J. Am. Chem. Soc.*, **73**, 2857 (1951).

[15] U. S. Patent 2,802,033 (1957) to E. I. du Pont de Nemours and Co.

The Reaction between Acenaphthenequinone and Phenyllithium

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The reaction between acenaphthenequinone and phenyllithium gave the expected *trans*-1,2-diphenyl-1,2-acenaphthenediol in low yields as well as four other solid products. Two of these were known compounds. The structures of one of the other products (II) and of several new compounds related to it have been established. II is the result of the unusual 1,4-addition of phenyllithium to an aryl ketone.

The reaction between acenaphthenequinone and phenylmagnesium bromide gave *trans*-1,2-diphenyl-1,2-acenaphthenediol in 81% yield.[1] In the reactions of other quinones with organometallic reagents,[2] better yields of 1,2-addition products were obtained by the use of phenyllithium rather than phenylmagnesium bromide. The present study shows that acenaphthenequinone behaved more like phenanthrenequinone[3] and gave the *trans*-1,2-diphenyl-1,2-acenaphthenediol in poor yields, 10–28%, as well as several other solid products and a dark oil from which no more solid could be isolated either by crystallization or by chromatography. Naphthalic anhydride (1–6%) was isolated from five of the twenty-five reactions which were carried out. Fourteen of the reactions gave the lactone of 1-(diphenylhydroxymethyl)-8-naphthoic acid (I, 7–22%). These compounds were identified by comparison with known samples.[4] Four of the reactions gave small amounts of a lactone melting at 176°, which has not

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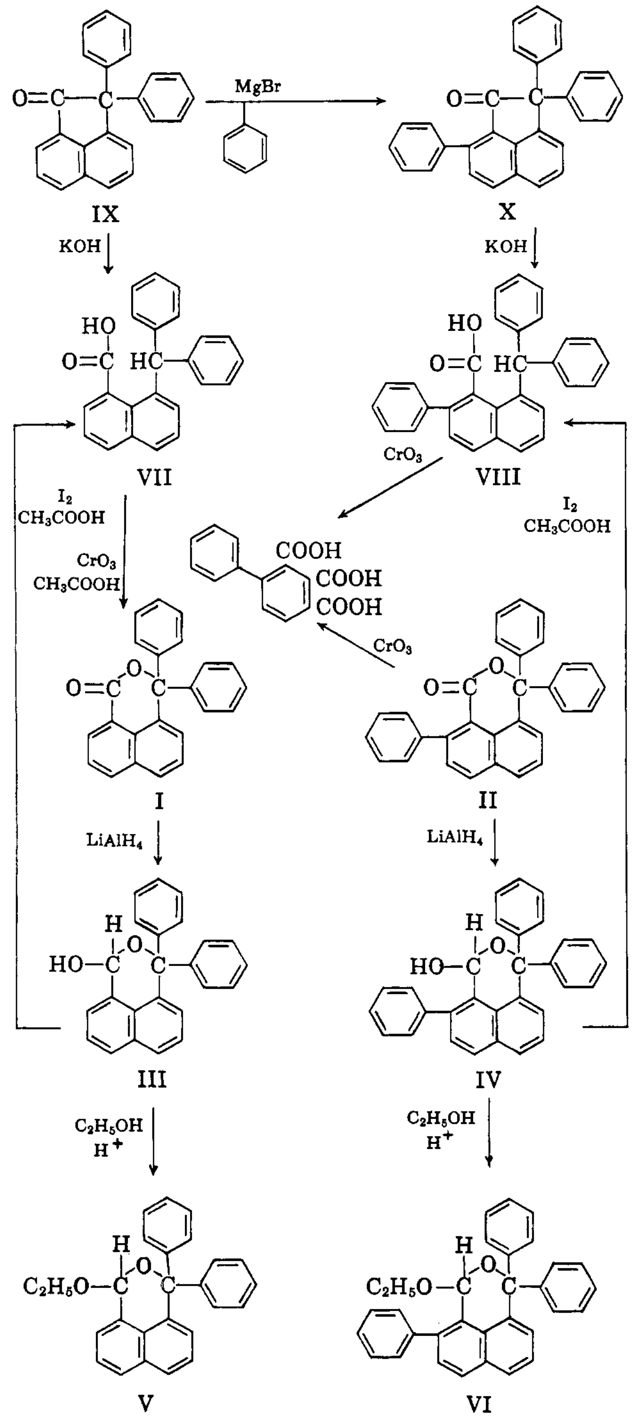
[1] P. D. Bartlett and R. F. Brown, *J. Am. Chem. Soc.*, **62**, 2927 (1940).

[2] H. M. Crawford, *ibid.*, **61**, 3310 (1939); **70**, 1081 (1948); H. M. Crawford and M. McDonald, *ibid.*, **71**, 2681 (1949).

[3] H. M. Crawford, M. Lumpkin, and M. McDonald, *ibid.*, **74**, 4087 (1952).

[4] G. Wittig, M. Leo, and W. Wiemer, *Ber.*, **64**, 2405 (1931).

Chart I

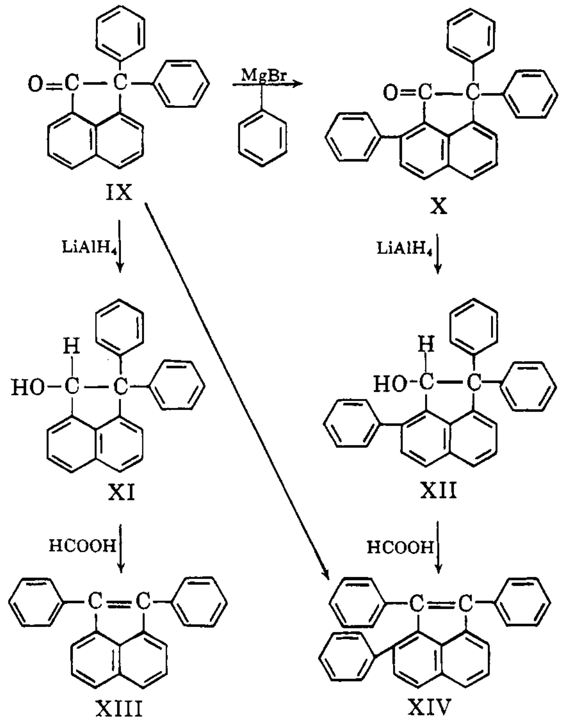


been completely identified. Ten of the reactions gave 1–30% of a compound which has been identified as the lactone of 1-(diphenylhydroxymethyl)-7-phenyl-8-naphthoic acid (II). The lactone II was identified by infrared and nuclear magnetic resonance spectra and by the similarity of a series of compounds related to it and another series of known compounds related to the lactone I.

In Chart I, all of the compounds with odd numbers were already known and were made by the methods which have been described. All of the compounds with even numbers, except X, are described for the first time.

The infrared spectra of corresponding compounds were compared and in every case they showed marked similarities.

In one attempt to make X from IX, the only product (48%) was a bright orange-red compound XIV, which was made later from IX, isolating and identifying the intermediates X and XII.



Again the infrared spectra of the corresponding compounds were very similar.

Experimental

Melting points are uncorrected.

Acenaphthenequinone was prepared in 50% yields by the oxidation of acenaphthene.[5]

The Reaction between Acenaphthenequinone and Phenyllithium.—As in other studies of this type[2,3] the quantities of reactants and the method of procedure were varied. The best yields of solid products were obtained by adding 0.05 mole of quinone suspended in ether, to 0.125 mole of phenyllithium in ether. After standing overnight, the organometallic product was decomposed with cold ammonium chloride solution. The ether layer was allowed to evaporate slowly, and successive crops of solid were removed and recrystallized. After no more solid could be separated from the heavy, dark oils, a benzene solution of the oil was poured onto a column of alumina. Successive portions of petroleum ether (b.p. 60–70°), ethyl acetate, and methanol were used to elute material from the column. In some cases the first ether solution was chromatographed immediately with no difference in the results. Any solids resulting from the evaporation of the various fractions were crystallized and identified. *trans*-1,2-Diphenyl-1,2-acenaphthenediol was obtained in yields varying from 10 to 28%. No *cis* diol was isolated from any of the twenty-five reactions. In five of the reactions 1–6% of naphthalic anhydride was obtained. Fourteen of the reactions gave the known lactone of 1-(diphenylhydroxymethyl)-8-naphthoic acid (I). Its identity was established by mixture melting point with a known sample of the lactone, prepared from naphthalic anhydride and phenyllithium.[4]

Two other solids were isolated, but never from the same reaction; the 176° lactone was obtained four times in yields of 3–15%, and 179° lactone II, was obtained ten times in yields of 1–30%.

The 176° Lactone.—This compound crystallized from methanol in small, colorless needles. It gave no 2,4-dinitrophenylhydrazone or oxime. It gave no color and was recovered unchanged after heating with hydrogen chloride in glacial acetic acid. It was recovered unchanged after heating with Lucas' reagent or

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(5) C. S. Maxwell and C. F. H. Allen, *Org. Syn.*, **24**, 1 (1944).

with iodine in glacial acetic acid. It depressed the melting point of known samples of the *cis* diol melting at 174–176°; of IX melting at 173–174°; of the monoethyl ether of the *cis* diol melting at 176.5–177.5° (kindly supplied by R. F. Brown[6]); and of 1,2,2-triphenyl-1-acenaphthenol melting at 167–169°. The 176° compound is soluble in aqueous potassium hydroxide from which it was recovered by treatment with hydrochloric acid. This indicates a lactone structure. Treatment with phenyllithium gave biphenyl as the only identifiable product. The infrared spectrum shows absorption at 3.4, 3.5, 5.8, and 8.6 μ in addition to the bands due to monosubstituted benzenes. The nuclear magnetic resonance spectrum indicates a $-CH_2-$ group, a large number (19–27) of aromatic protons, and three others not on a naphthalene or benzene ring.

Anal. C, 87.2; H, 5.4; mol. wt., 373 (in benzene).

Lactone of 1-(Diphenylhydroxymethyl)-7-phenyl-8-naphthoic Acid (II).—This lactone is much less soluble than the 176° lactone. It can be crystallized from ethanol, benzene, or ethyl acetate as colorless prisms melting at 179–180°. It gave no carbonyl derivatives, gave no color with hydrogen chloride in acetic acid, and was recovered unchanged after heating with sulfuric acid in acetic acid. It was not soluble in alcoholic potassium hydroxide. This agrees with the behavior of the known lactone I to which it corresponds. (It reacted with phenyllithium to give a very small amount of a compound which melted at 255° and contained 86.93% C and 5.53% H.) The infrared spectra of I and II were run on the same paper. Both showed no absorption in the hydroxyl region; carbonyl absorption at 5.7, 8.2, and 9.1 μ, and the rest of the spectra were very similar. The n.m.r. spectrum of II is consistent with the structure assigned.

Anal. Calcd. for $C_{30}H_{20}O_2$: C, 87.35; H, 4.9; mol. wt., 412. Found: C, 86.62; H, 5.2; mol. wt., 415 (in camphor).

Oxidation of II with chromium trioxide in glacial acetic acid gave benzoic acid, benzophenone (identified as the 2,4-dinitrophenylhydrazone), and biphenyl-2,3,4-tricarboxylic acid melting at 208–209° (lit.[7] 210°). The same acid was obtained by the oxidation of VIII. The infrared spectrum of the acid, in carbon disulfide, showed absorption at 13.4 and 14.3 μ for a monosubstituted benzene, as well as the absorption for the carboxyl groups.

1-Hydroxy-3,3-diphenyl-1*H*,3*H*-9-phenylnaphtho[1,8-*c*,*d*]pyran (IV).—Compound II (2 g.) was refluxed for 4 hr. with 1.5 g. of lithium aluminum hydride in 50 ml. of ether. The excess lithium aluminum hydride was decomposed with water and the ether extract allowed to evaporate. Treatment of the resulting glass with methanol and diisopropyl ether gave 1.9 g. (90%) of white solid. Recrystallization from ethanol gave IV, m.p. 198.5–199.5°. For comparison, the lactone I was reduced by a similar procedure and product III was obtained. It melted at 164–165° (lit.[8] 166–167.5°). Both III and IV showed infrared absorption at 2.8 μ and none in the carbonyl region.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 87.28, H, 5.7.

1-Ethoxy-3,3-diphenyl-1*H*,3*H*-9-phenylnaphtho[1,8-*c*,*d*]pyran (VI).—This acetal was prepared very easily by treating the hydroxy compound IV in ethanol with a trace of acid. In fact, if the excess lithium aluminum hydride (after the reduction of II) was decomposed with ethyl acetate, or the aluminum hydroxide sludge was dissolved in hydrochloric acid, the first crop of crystals separating was the hydroxy compound IV, and later the acetal VI was obtained. Crystallization from ethanol gave small colorless prisms melting 150–151°. The corresponding acetal V[8] was prepared in the same way and melted at 197–198°. Both acetals showed infrared absorption in the ether region, 8.5–10.0 μ, and none in the hydroxyl or carbonyl regions.

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.84; H, 5.92. Found: C, 86.6; H, 6.0.

1-(Diphenylmethyl)-7-phenyl-8-naphthoic Acid (VIII).—The hemiacetal IV (0.3 g.) was refluxed for 35 min. with 0.2 g. of iodine in 25 ml. of acetic acid as described for the preparation of VII from III. The solution was poured into water containing a small amount of sodium bisulfite. The solid (0.26 g., 87%) crystallized from ethanol as shiny, colorless plates and melted at 259–260°. This same acid was obtained by opening the ketone ring of X by refluxing it with potassium hydroxide in diethylene glycol. Refluxing with potassium hydroxide in ethanol did not open this ring.[9] The corresponding acid VII was prepared according to the method of Zsuffa[9] by refluxing 2.0 g. of IX with 10 g. of potassium hydroxide, 10 ml. of water, and 100 ml. of ethanol for 4 hr. Dilution of the solution with water gave a quantitative yield of the acid VII. One crystallization from ethanol and ethyl acetate gave a white solid, m.p. 228–229°. Both acids (VII and VIII) showed infrared absorption at 3–3.5, 5.85, and 8.2 μ. Letsinger and Lansbury[8] made the lactone I by oxidation of the acid VII. A similar oxidation of the acid VIII by chromium trioxide gave biphenyl-2,3,4-tricarboxylic acid, identical with the acid obtained by the oxidation of the lactone II.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.8; H, 5.5.

1,1,3-Triphenyl-2-acenaphthenone (X).—This ketone was described by Fuson and Griffin[10] as resulting from a forced reaction of phenylmagnesium bromide on 2,2-diphenyl-1-acenaphthenone (IX). Their product melted at 160–161° and its color was not mentioned. The ketone IX was made by the usual pinacol rearrangement of *trans*-1,2-diphenyl-1,2-acenaphthendiol. In the first attempt to make the ketone X (using 9.6 g., 0.03 mole, of the ketone IX and 0.17 mole of phenylmagnesium bromide and chromatographing on alumina) the only product obtained was 5.5 g. (48%) of a bright orange-red solid XIV which is described later. The melting point was 145–146°. Another attempt, using 3.9 g. of IX, gave 1.02 g. of a pale yellow solid, m.p. 145–146°, which showed infrared absorption at 5.7 and 5.8 μ. A later crop of crystals melted at 157–158°. A third attempt, using 3.8 g. of IX, was chromatographed at once and gave 2.1 g. (45%) of material first melting at 157–158°, identical with the material from the second attempt. After several recrystallizations from ethanol and ethyl acetate, the shiny lemon yellow plates melted at 168.5–169°. The infrared absorption spectra of IX and X are very similar, showing carbonyl absorption at 5.85 μ. A mixture melting point of ketone X with a sample supplied by Dr. Griffin[10] was 161–169°.

Anal. Calcd. for $C_{30}H_{20}O$: C, 90.88; H, 5.09. Found: C, 90.6; H, 5.2.

2-Hydroxy-1,1,3-triphenylacenaphthene (XII).—The yellow ketone X (0.3 g.) was refluxed for 1 hr. with 0.2 g. of lithium aluminum hydride in 30 ml. of ether. Excess lithium aluminum hydride was decomposed with ethyl acetate. The ether extract gave a quantitative yield of colorless needles of the alcohol XII melting 172–173°. The infrared spectra of this alcohol and the corresponding alcohol XI showed identical absorption at 2.8 μ and none in the carbonyl region.

Anal. Calcd. for $C_{30}H_{22}O$; C, 90.42; H, 5.57. Found: C, 90.4; H, 5.6.

1,2,3-Triphenylacenaphthylene (XIV).—This hydrocarbon was prepared by heating the alcohol XII with formic acid for 15 min. on the steam bath. The solution was colorless at first but quickly became yellow, then orange. The solution was diluted with water, and the resulting solid was separated and crystallized from ethanol and ethyl acetate. It separated as bright orange-red needles and melted at 143–145°. The mixture melting point was 144–145° with the orange-red hydrocarbon described earlier. The infrared spectra of this hydrocarbon and of the red hydrocarbon XIII (made according to the directions of Letsinger and Lansbury[8] from XI) were practically identical.

Anal. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30; mol. wt., 380. Found: C, 94.8; H, 5.3; mol. wt., 385.

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(8) R. L. Letsinger and P. T. Lansbury, *J. Am. Chem. Soc.*, **81**, 938 (1959).

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(10) R. C. Fuson and G. W. Griffin, *J. Am. Chem. Soc.*, **79**, 1941 (1957).