rubbery substance, weighed 0.13 g. for a total conversion of 23%. An infrared spectrum of the soluble polymer (run as a film pressed out from the melt) had the following absorption bands: 2950 (broad); 1650 (w); 1450 (s); 1380 (s); 1070 (w); 965 (s); 910 cm.$^{-1}$.

*Anal.* Calcd. for $C_9H_{14}$: C, 88.45; H, 11.55. Found: C, 83.86; H, 9.81; ash, 1.8.

**Polymerization of *cis*-1,3,8-Nonatriene.**—A small serum capped vial was charged by means of a microhypodermic syringe with 0.0028 g. (0.07 mmole) of titanium tetrachloride and 0.08 ml. of heptane containing 0.013 (0.11 mmole) of triethylaluminum in a drybox under a dry nitrogen atmosphere. The vial was further charged with 1.0 ml. of high purity hexane and 0.61 g. (5 mmoles) of the triene, shaken well, and allowed to stand at 25° in the drybox for 72 hr. The mixture was then poured into methanol and filtered on a sintered glass disk, the residue was washed with methanol. The residue was a tough plastic substance which could not be ground up. The material was placed in a Soxhlet extractor and extracted for 2 days with hot benzene. The benzene extract was then poured into methanol causing less than a milligram of solid to be precipitated. The solid which was recovered from the extraction thimble and dried appeared unchanged. A second attempt to polymerize this monomer at a concentration of 10% in hexane gave essentially the same results. The cross-linked material which was insolube in several organic solvents was obtained in the amount of 0.05 g. (8.5%) and was not investigated any further.

One attempt was made to polymerize this monomer in bulk with 0.1% azobisisobutyronitrile and was not successful after 1 week at 80°.

**Polymerization of 1,3,7-Octatriene.**—This reaction was carried out in the same manner as was described for the nonatriene. The reaction charge consisted of the same molar proportions of catalyst and monomer. The polymerization was conducted for 18 hr. after which the polymer was worked up in the previously described manner. The yield of polymer was 0.5 g. (22.8% conversion), 0.12 g. (24.0%) of which was soluble in hot benzene. The soluble polymer was a soft plastic material which flowed on standing and had an intrinsic viscosity of 0.09 (1.120 and 0.560 g./100 ml. in benzene at 30°).

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# Synthesis and Cyclopolymerization of 1,8-Divinylnaphthalene

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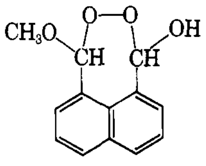
1,8-Divinylnaphthalene has been synthesized and polymerized to give soluble, low molecular weight polymers. The monomer was synthesized by the reaction of 1,8-naphthalenedialdehyde hydrate with triphenylphosphinemethylene. Several other 1,8-naphthalene compounds have been synthesized during the investigation.

It has been shown that nonconjugated diolefins will undergo an intramolecular–intermolecular cyclic propagation during polymerization giving a polymer that contains carbocyclic rings along the backbone of the chain.[1,2] Considering these results and the mechanism proposed for cyclic polymerization,[3] the position of the vinyl groups in 1,8-divinylnaphthalene (I) should be ideally situated for a cyclic propagation reaction since the vinyl groups are held rigidly with a minimum of free rotation. In addition, group interaction in 1,8-naphthalene compounds is very common and formation of a six-membered ring seems to be preferred in cyclopolymerization.[4]

The first approach to the synthesis of 1,8-divinylnaphthalene was through dehydration of 1,8-bis-(1-hydroxyethyl)-naphthalene (II). This compound was synthesized according to the reactions depicted in Chart I. Hydrolysis of 1,2-dibromoacenaphthene (IV) produced a mixture of isomers of 1,2-dihydroxyacenaphthene (V). The reaction of lead tetraacetate with diol V is reported[5] to give 1,8-naphthalenedialdehyde as the hydrate but no yields were given. It was found, however, that when diol V reacts with lead tetraacetate the major product was a polymeric material rather than the crystalline 1,8-naphthalenedialdehyde hydrate (VI). The polymeric material was found to react with *p*-nitrophenylhydrazine to give good yields of the reported hydrazone of VI, while the reaction with base gave a good yield of 1,8-naphthalide (VII).



VIII

Since the reduction of 3-hydroxy-7-methoxy-4,5,6-(1,8-naphtho)-1,2-dioxacycloheptane (VIII) formed from ozonolysis of acenaphthylene (III) has been reported[6] to produce an oil which also affords the same *p*-nitrophenylhydrazone that is obtained from VI, an investigation of this method of the preparation of VI was undertaken.

When III was allowed to react with an ozone–oxygen mixture the major product after reduction was 1,8-naphthaldehydic acid (IX).[6] If the hemiperacetal VIII, which precipitates from the ozonolysis solution, was isolated, and subsequently reduced with potassium iodide in methanol, a 16.5% yield of VI could be obtained after hydrolysis with dilute acid. Ozonolysis of III by ozone in a nitrogen stream[7] afforded a 73.5% yield of VI compared to the 16.5% yield obtained using the oxygen–ozone mixture.

The structure, 2,6-dihydroxy-3,4,5-(1,8-naphtho)oxacyclohexane (VI) was assigned on the basis of the in-

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[1] C. S. Marvel, *J. Polymer Sci.*, **48**, 101 (1960).

[2] G. B. Butler, *ibid.*, **48**, 279 (1960).

[3] W. E. Gibbs and J. T. Murry, *ibid.*, **58**, 1211 (1962).

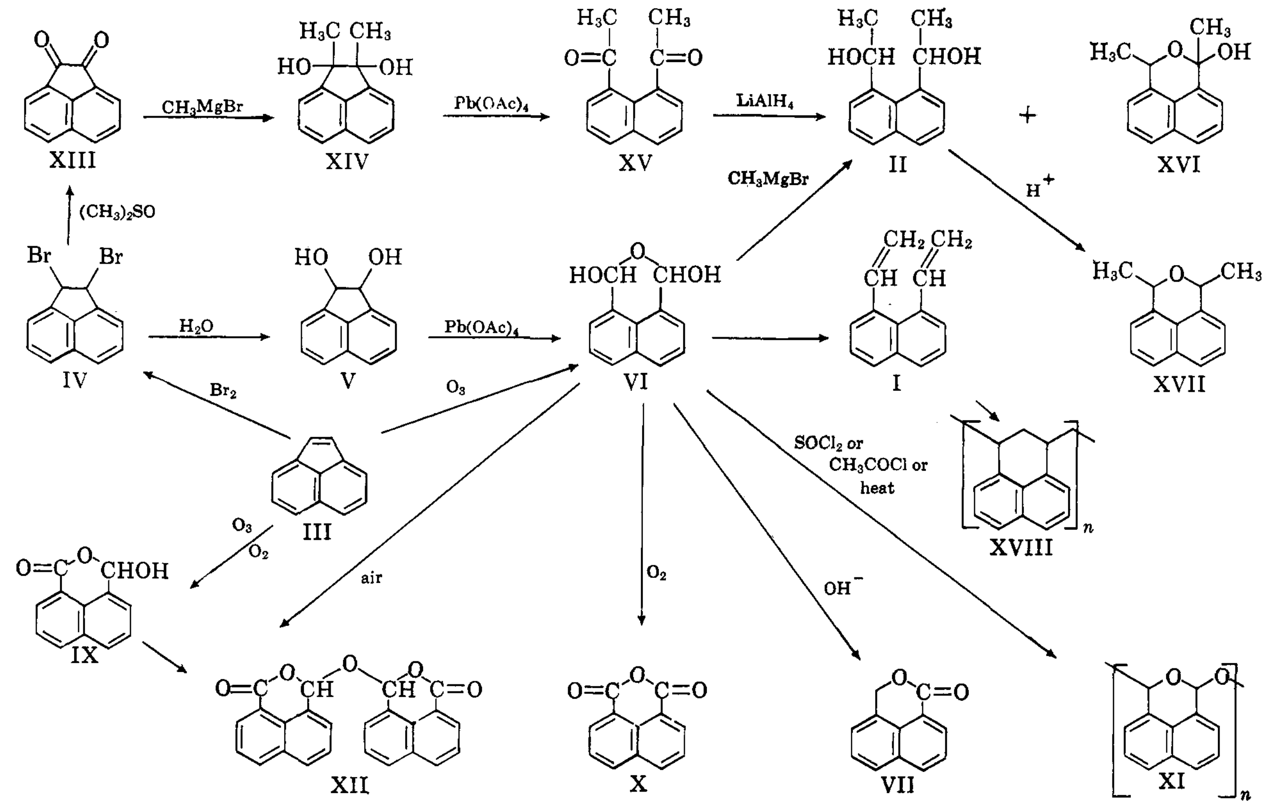
[4] C. S. Marvel and E. J. Gall, *J. Org. Chem.*, **25**, 1784 (1960).

[5] R. Criegee, L. Kraft, and B. Rank, *Ann.*, **507**, 194 (1933).

[6] R. H. Allighan, M. F. Tarker, Jr., and M. H. Wilt, *J. Org. Chem.*, **26**, 1379 (1961).

[7] G. A. Cook, A. D. Kiffer, C. V. Kumpp, A. H. Molik, and L. A. Spence, *Advan. Chem. Ser.*, **21**, 44 (1959).

CHART I



frared spectrum which shows no carbonyl stretching, the elemental analysis, and also isolation of the two diastereoisomers of VI. The two diastereoisomers were shown to be the same compound by the formation of identical *p*-nitrophenylhydrazones, by the air oxidation to 1,8-naphthalic anhydride X and by an internal Cannizzaro reaction to form VII.

Attempts to dehydrate VI did not result in the isolation of monomeric 1,8-naphthalenedialdehyde. The compound was dehydrated readily on heating or on treatment with thionyl chloride or acetyl chloride in benzene but the product was a white polymeric material with a very high melting point. The degree of solubility of the polymer in benzene seemed to depend on the amount of oxygen present, since solutions of the polymer would precipitate insoluble polymer on standing. Since the elemental analysis showed this to be anhydrous aldehyde and the infrared spectrum showed maxima due to carbon–oxygen single bond stretching and no carbonyl moiety, the structure XI, containing an oxacyclohexane recurring unit, was assigned to the polymer. The gradual insolubility of the polymer may be attributed to attack by oxygen on the benzyl hydrogens to afford a cross-linked polymer. No attempts were made to exclude oxygen completely.

Attempts to recrystallize VI from the common organic solvents (benzene, chloroform, etc.) resulted in decomposition of VI to give a dimer. In addition, when VI was heated at the reflux temperature in air using xylene as a solvent, bis-1,8-(naphthaldehydic acid pseudoanhydride (XII) was formed.

The dialdehyde VI reacted with methylmagnesium bromide to give only a 12.5% yield of one diastereoisomer of dialcohol II. Since the yield of II was quite low in this method of synthesis, another route was chosen. Preparation of 1,2-acenaphthenequinone (XIII) by oxidative solvolysis of dibromide IV with dimethyl sulfoxide,[8] conversion of the quinone XIII to 1,2-dihydroxy-1,2-dimethylacenaphthene (XIV) with methylmagnesium bromide,[9] and lead tetraacetate oxidation of XIV provided 1,8-diacetylnaphthalene (XV).[5] Finally, the lithium aluminum hydride reduction of XV in refluxing ether gave two products; another diastereoisomer of II and 2,6-dimethyl-2-hydroxy-3,4,5-(1,8-naphtho)oxacyclohexane (XVI). Under milder conditions, higher yields of XVI were obtained. In a separate reduction reaction, XVI was converted to the diol II.

The dehydration of II with several different acid catalysts was attempted, but in all cases a mixture of the diastereoisomers of the ether, 2,6-dimethyl-3,4,5-(1,8-naphtho)oxacyclohexane (XVII) was formed in a 60–70% yield. This is not surprising since other *peri*-substituted naphthalene compounds have been found to react in a similar manner.[10]

Since dehydration of diol II did not give the desired 1,8-divinylnaphthalene, the reaction of the aldehyde hydrate with triphenylphosphinemethylene[11] was considered. It has been shown that *o*-phthalaldehyde reacts with triphenylphosphinemethylene to afford a 75% yield of *o*-divinylbenzene.[12] When the solid aldehyde hydrate (VI) was added to a refluxing ether solution of triphenylphosphorous methylene most of the aldehyde was recovered unchanged but when VI was dissolved in hot benzene and the hot benzene solution added to the triphenylphosphinemethylene solution, a 70% yield of

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[8] N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).

[9] N. Maxim, *Bull. soc. chim. France*, [4] **45**, 1137 (1929).

[10] R. L. Letsinger, J. A. Gilpin, and W. J. Vullo, *J. Org. Chem.*, **27**, 672 (1962).

[11] G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1092 (1954).

[12] G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

1,8-divinylnaphthalene (I) was obtained. This difference in reactivity may be due to decomposition of the hydrate VI in benzene giving the anhydrous aldehyde which reacts readily with the Wittig reagent before polymerization of the aldehyde occurs.

1,8-Divinylnaphthalene (I) was polymerized using several different catalysts (for results, see Table I).

TABLE I

| Catalyst | % conversion | Mol. Wt. | $[\eta]^a$ |
|---|---|---|---|
| Benzoyl peroxide (bulk) | 65.9 | 1620 | 0.349 |
| Potassium persulfate (emulsion) | 2.9 | 1760 | |
| $TiCl_4 \cdot Al(i\text{-}Bu)_3$ | | | |
| in heptane | 0.8 | | |
| in benzene | .9 | | |

[a] The inherent viscosity was obtained from a solution of 0.26 g. of polymer in 100 ml. of benzene at 25.0°.

The polymerization of I in bulk by a free radical initiator gave the highest conversion to polymer. The emulsion polymerization with a free radical initiator and polymerization with a Ziegler-type catalyst gave low yields of polymer. The very low per cent conversion to polymer obtained with the titanium tetrachloride and aluminum triisobutyl catalysts is surprising but may be due to formation of a $\pi$-complex between the catalyst surface and I which is stable enough to resist polymerization.[13]

The cyclic recurring unit (XVIII) was assigned to the polymer on the basis of (1) the absence of any maxima in the infrared spectrum which could be ascribed to vinyl unsaturation, (2) the complete solubility of the polymer in common organic solvents, and (3) the elemental analysis.

The molecular weight of the polymer formed in bulk by free radical initiation is not very high. Since 1-vinylnaphthalene undergoes polymerization by a radical mechanism to a high molecular weight polymer, there is reason to believe that neither is there a special stability conferred on the naphthyl radical by the presence of a naphthalene nucleus, nor does chain transfer limit the molecular weight, except as might be affected by the steric shielding of the bulky 2,3-dihydrophenalene system. Efficient propagation (and termination by coupling or disproportionation) may be severely hindered by the steric requirements of the approach of monomer (or another chain) to a terminal 2,3-dihydrophenalene radical, so that termination by chain transfer becomes important by comparison with propagation. Models of the polymer show that the bulk of the phenalene portion imparts limited flexibility to the chain; this is supported by the fact that the polymer has an unusually high inherent viscosity for such a low molecular weight.

## Experimental[14]

**1,2-Acenaphthenequinone (XIII).**—A solution of 10 g. of 1,2-dibromoacenaphthene,[15,16] m.p. 125–125.7°, in 250 ml. of dimethyl sulfoxide was heated at 65° for 3 days with stirring. Dimethylsulfide and hydrogen bromide were evolved slowly. The red solution was poured into 1 l. of water and the precipitate which formed was recrystallized from absolute ethanol to give 2.9 g. (49.5%) of 1,2-acenaphthenequinone, m.p. 252–255° (lit.[17] m.p. 259–260°). The melting point of a mixture of this product and an authentic sample was not depressed. The yield in several runs varied from 49.5–55%.

**1,8-Diacetylnaphthalene (XV).**—The following procedure was found to be more satisfactory for the preparation of XV than that reported.[5]

To a solution of 17.0 g. (0.079 mole) of 1,2-dimethyl-1,2-dihydroxyacenaphthene (XIV)[9] in 1 l. of thiophene-free benzene was added 35.2 g. (0.079 mole) of lead tetraacetate and the mixture was stirred for 12 hr. at room temperature. To this mixture was added 500 ml. of water to remove lead diacetate. The benzene layer was separated and the water solution was extracted with benzene. The benzene was removed under reduced pressure to give light yellow crystals, which were recrystallized from aqueous acetone to give 15.2 g. (90.5%) of XV, m.p. 169–172° (lit.[5] m.p. 171–172°).

**1,8-Bis-(1-hydroxyethyl)-naphthalene (II).** (1) **By the Reduction of XV.**—To a mixture of 3.8 g. (0.1 mole) of lithium aluminum hydride in 1 l. of refluxing dry ether was added under nitrogen, 10.0 g. (0.047 mole) of finely powdered XV in small portions over a period of 30 min. The mixture was heated at the reflux temperature for 3 hr. after which the complex was decomposed by adding 4 ml. of water, 4 ml. of 30% sodium hydroxide, and finally 12 ml. of water. The mixture was filtered and the residue was extracted with ether. The ether was evaporated at reduced pressure to give a light yellow oil which produced white crystals when cyclohexane was added. The product was recrystallized from a 1:4 mixture of benzene–cyclohexane to give 4.6 g. (44.9%) of II, m.p. 123–125°.

*Anal.* Calcd. for $C_{14}H_{16}O_2$: C, 77.77; H, 7.40. Found: C, 77.51; H, 7.55.

The infrared spectrum (Nujol mull) showed maxima of 3480 (OH str.) and 1060 cm.$^{-1}$ (C–O str.).

**2,6-Dimethyl-2-hydroxy-3,4,5-(1,8-naphtho)oxacyclohexane XVI.**—Further evaporation produced 2.44 g. (24.2%) of material which was recrystallized from cyclohexane to give pure product (XVI), m.p. 107–108°.

*Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.51; H, 6.54. Found: C, 78.64; H, 6.72.

*p*-**Nitrophenylhydrazone** had m.p. 169–170.5°.

*Anal.* Calcd. for $C_{20}H_{10}N_3O_3$: C, 68.75; H, 5.45; N, 12.02. Found: C, 68.88; H, 5.21; N, 12.33.

The infrared spectrum of XVI (Nujol mull) showed maxima at 3335 and 1063 cm.$^{-1}$ which is consistent with the cyclized structure. Compound XVI could be prepared in higher yields by the following procedure. To a mixture of 6.5 g. of lithium aluminum hydride and 500 ml. of absolute ether, under nitrogen, was added dropwise a solution of 22.60 g. (0.106 mole) of XV in a 1:1 mixture of benzene–ether (1.5 l.). The mixture was allowed to stir for 12 hr. at room temperature and the complex was decomposed by adding 100 ml. of concentrated hydrochloric acid in 300 ml. of water. The organic layer was separated and the solvents were removed under reduced pressure to give a yellow oil. The oil was dissolved in a 1:1 benzene–hexane mixture and cooled to give 9.79 g. of material, m.p. 100–107°. Further evaporation produced 3.85 g. of additional product, m.p. 108–113°. The combined yield was 59.4%. The infrared spectrum showed these products to be a mixture of isomers of XVI. Recrystallization of the first fraction from hexane produced one pure isomer, m.p. 105–107°. The other isomer was not isolated.

**1,8-Bis(1-hydroxyethyl)-naphthalene (II).** (2) **By Reduction of XVI.**—To 1.75 g. (0.0233 mole) of lithium aluminum hydride in 250 ml. of dry ether heated to the reflux temperature was added 5.02 g. (0.0234 mole) of XVI, m.p. 107–108°, in small portions over a period of 30 min. The mixture was heated for 30 min. longer after which time the complex was decomposed. The ether solution was filtered and the ether was evaporated to a small volume. Addition of hexane and a small amount of

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[13] H. Uelzmann, *J. Org. Chem.*, **25**, 671 (1960).

[14] All melting points are corrected. The infrared spectra were obtained from a Perkin-Elmer Model 21 infrared spectrophotometer. The molecular weights were determined on a Mechrolab Model 301 vapor pressure osmometer using chloroform as a solvent.

[15] M. Blumenthal, *Ber.*, **7**, 1093 (1874).

[16] A. G. Anderson and R. G. Anderson, *J. Am. Chem. Soc.*, **77**, 6610 (1955).

[17] C. F. H. Allen and J. A. VanAllan, "Organic Syntheses," Coll. Vol III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 1.

benzene produced 1.74 g. (34.6%) of II, m.p. 121–124°. Further evaporation of the solvent produced only starting material.

**2,6-Dimethyl-3,4,5-(1,8-naphtho)oxacyclohexane (XVII).** (1) **With Concentrated Hydrobromic Acid.**—A mixture of 1.00 g. (0.00462 mole) of II, m.p. 121–123°, and 100 ml. of concentrated hydrobromic acid was heated at such a rate that the hydrobromic acid was distilled slowly. The white solid which solidified on the surface of the distillate on cooling was removed to give 0.64 g. (70.2%) of material, m.p. 76–82°. Repeated recrystallization of this material from hexane afforded two pure isomers of XVII.

*Anal.* Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.02. Found for the isomer melting at 88–90°: C, 84.82; H, 7.02. Found for the isomer melting at 78–82°: C, 84.62: H, 7.11.

The infrared spectra of both isomers showed no unsaturation and only maxima characteristic of the ether moiety.

(2) **With Aniline Hydrobromide.**—A mixture of 2.00 g. (0.00924 mole) of II, m.p. 121–123°, 0.50 g. of aniline hydrobromide, and 0.10 g. of hydroquinone was heated for 5 min. at 130° under nitrogen. The pressure was reduced and the material was distilled; b.p. 108–118° (0.2 mm.). The product was recrystallized from hexane to give 1.10 g. (60.2%) of a mixture of isomers of XVII, m.p. 80–92°. The infrared spectrum of this mixture was identical to that of the mixture of isomers obtained from the hydrobromic acid reaction.

(3) **With Potassium Bisulfate.**—Three grams (0.0138 mole) of II, m.p. 147–148°, 0.3 g. of hydroquinone, and 0.3 g. of freshly fused and powdered potassium bisulfate were heated at 200° under nitrogen. The system was evacuated to 0.24 mm. and a white solid distilled; b.p. 118–128° (0.24 mm.). The material was recrystallized from hexane to give 1.83 g. (65.5%) of XVII, m.p. 70–86°. The infrared spectrum of this mixture was identical to that of the mixture of isomers obtained from the reaction of II with hydrobromic acid.

**1,8-Naphthalene Dialdehyde Hydrate (VI). Ozonolysis of Acenaphthylene.** (a) **With an Ozone–Nitrogen Mixture.**—A mixture of ozone–oxygen was passed through a tube containing 80 g. of Davidson PA 400 silica gel cooled to −78° until 0.1 mole of ozone had been absorbed.[7] The ozone was desorbed by sweeping the tube with a slow nitrogen stream while the tube was slowly raised out of the cooling bath. The stream of nitrogen containing 0.1 mole of ozone was passed into a solution of 15.0 g. (0.099 mole) of acenaphthylene (III) in 300 ml. of methanol cooled to −30° over the 30-min. period required to desorb the ozone. The reaction was stopped just before the yellow color of the acenaphthylene completely disappeared. The cooling bath was removed and 46 ml. of glacial acetic acid and 46 g. of potassium iodide was added. The solution was allowed to stir for 1 hr. while it warmed to room temperature; then 10% sodium thiosulfate solution was added until the iodine color was discharged. The solution was concentrated under reduced pressure until most of the methanol was removed. The residue was extracted with ethyl acetate and the ethyl acetate was removed under reduced pressure. The oily residue was heated with a solution of 15 ml. of concentrated hydrochloric acid in 1.5 l. of water at the reflux temperature for 3 hr. The solution was filtered and cooled to give 14.0 g. (73.5%) of fine, white needles, m.p. 135–140° dec. Careful recrystallization from hot water gave a pure isomer of VI, m.p. 140–141.5° dec. (lit.[5] m.p. 130–130.4°).

*Anal.* Calcd. for $C_{12}H_{10}O_3$: C, 71.26; H, 4.99. Found for this isomer: C, 70.93; H, 5.01.

If the recrystallization was not carried out with vigorous stirring and slow heating of the water a mixture of isomers of VI and some insoluble material formed. Fractional recrystallization of the mixture of isomers from water gave the other isomer, m.p. 106–107° dec.

*Anal.* Found: C, 71.44; H, 5.25.

Both isomers reacted with *p*-nitrophenylhydrazine to form identical derivatives, m.p. 227–229° dec. (lit.[5] m.p. 227°). The infrared spectra of both isomers of VI showed maxima at 3330 (OH str.), 1075 and 1011 cm.$^{-1}$ (C–O str.), which is consistent with the cyclized structure 2,6-dihydroxy-3,4,5-(1,8-naphtho)oxacyclohexane (VI).

(b) **With an Oxygen–Ozone Mixture.**—A mixture of oxygen–ozone was passed into a solution of 20 g. (0.132 mole) of III in 400 ml. of methanol and cooled to −30°. Slightly less than an equivalent amount of ozone was passed in over a period of 4 hr. The white precipitate which had formed was collected, suspended in a solution of 125 ml. of methanol and 16 ml. of glacial acetic acid, and 16 g. of potassium iodide was added. The mixture was stirred for 1 hr. at room temperature, after which time a solution of 10% sodium thiosulfate was added until the iodine color disappeared. The methanol was removed under reduced pressure and the water–oil mixture was extracted with benzene. The benzene extracts were taken to dryness under reduced pressure and the residue was treated with a solution of 6 ml. of concentrated hydrochloric acid in 600 ml. of water. The mixture was heated at the reflux temperature for 3 hr., then filtered and cooled to give 4.4 g. (16.5%) of VI, m.p. 138–141° dec.

**1,8-Naphthaldehydic Acid (IX).**—A mixture of oxygen–ozone was passed into a solution of 40 g. (0.264 mole) of III in 150 ml. of carbon tetrachloride and 200 ml. of *t*-butyl alcohol cooled to −30° until 0.26 mole of ozone had been absorbed.[6] The solution was allowed to stand overnight and 40 ml. of glacial acetic acid and 40 g. of potassium iodide were added. After 1 hr. 10% sodium thiosulfate solution was added and the solution separated into two layers. The organic layer evaporated to dryness under reduced pressure to give white crystals which were recrystallized from water, and from benzene to give 26.3 g. (49.9%) of IX, m.p. 167–168° (lit.[18] m.p. 167–168°). A similar result was obtained using methanol as the solvent.

The *p*-nitrophenylhydrazone was prepared as follows. To a solution of 1 g. (0.00498 mole) of IX in 20 ml. of glacial acetic acid was added a solution of 1.8 g. of *p*-nitrophenylhydrazine in 40 ml. of ethanol and the solution heated on a steam bath for 1 hr. Cooling produced a red powder which was leached with ethanol then with benzene to give 1.62 g. (69.3%) of yellow powder, m.p. 217–218° dec.

*Anal.* Calcd. for $C_{24}H_{18}N_6O_5$: C, 61.27; H, 3.85; N, 17.87. Found: C, 61.19; H, 3.66; N, 17.83.

The infrared spectrum (Nujol mull) showed maxima at 3450 (N–H str.), 1663 (C=O str.), 1606 (C=N str.), and 1508 cm.$^{-1}$ (C–N str.).

**1,8-Naphthalene Dialdehyde Hydrate (VI). By Lead Tetraacetate Oxidation of V.**—A mixture of 19 g. (0.102 mole) of V, 50 g. (0.113 mole) of lead tetraacetate and 1.4 l. of benzene was heated at the reflux temperature for 3 hr. The mixture was cooled and 100 ml. of water was added. The benzene was removed from the organic layer under reduced pressure to give 9.0 g. of a light yellow, noncrystalline solid, m.p. 61–75°. The melting point of a mixture of the *p*-nitrophenylhydrazone derivative formed from this sample and the derivative of a sample of VI obtained from the ozonolysis was undepressed.

One gram of the noncrystalline polymeric aldehyde was heated at the reflux temperature with a solution of 3 ml. of concentrated hydrochloric acid in 250 ml. of water. The water solution was filtered and cooled to give 0.10 g. of a mixture of isomers of VI, m.p. 135–140° dec. The infrared spectrum of this material was identical to the spectrum of an authentic sample of VI.

**1,8-Naphthalide (VII).** (1) **From the Polymeric Aldehyde.**—To a solution of 1.0 g. of sodium hydroxide in 10 ml. of water was added 1.0 g. of the polymeric material obtained from the lead tetraacetate oxidation and the mixture was allowed to stand at room temperature for 24 hr. The solution was filtered and acidified with 5 ml. of glacial acetic to precipitate the product. Recrystallization from an ethanol–water mixture gave 0.6 g. of VII, m.p. 156–157° (lit.[18] m.p. 155–157°). The infrared spectrum showed the characteristic bands reported[6] for this compound.

(2) **From VI.**—A mixture of 0.40 g. of VI, m.p. 106–107°, and a solution of 1.5 g. of sodium hydroxide in 10 ml. of water was allowed to stand for 7 days at room temperature during which time all of VI had gone into solution. The solution was filtered and the filtrate was acidified with 11 ml. of concentrated hydrochloric acid. The acidic mixture was heated on a steam bath and enough methanol was added to dissolve the white precipitate which had formed. The solution was cooled to give 0.26 g. (71.2%) of VII, m.p. 155–157°. The melting point of a mixture of this material and the sample of VII obtained from the polymeric aldehyde was undepressed.

**1,8-Bis(1-hydroxyethyl)naphthalene (II). By the Reaction of VI with Methyl Magnesium Bromide.**—A solution of 5.00 g. (0.024 mole) of VI in 400 ml. of benzene was added, over a period of 2.5 hr., to a Grignard reagent prepared from 3 g. (0.123 g.-atom) of magnesium and 11.8 g. (0.123 mole) of methyl bromide in 350 ml. of ether. The mixture was heated at the reflux temperature for 12 hr. after which time the complex was decomposed by adding a dilute hydrochloric acid solution. The ether layer

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(18) R. C. Fuson and G. Munn, *J. Am. Chem. Soc.*, **71**, 1870 (1949).

was washed with sodium bicarbonate and water and the ether was removed at reduced pressure to give an oil. Addition of benzene produced 0.80 g. of white crystals, m.p. 142–144°. The material was recrystallized from a mixture of benzene-hexane to give 0.67 g. (12.5%) of a pure isomer of II, m.p. 149–150.5°.

*Anal.* Calcd. for $C_{14}H_{16}O_2$: C, 77.77; H, 7.40. Found: C, 77.53; H, 7.57.

The infrared spectrum was identical to the other diastereoisomer obtained from the reduction of XV.

**Dehydration of VI.** (1) **With Thionyl Chloride.**—To a mixture of 0.50 g. (0.0025 mole) of VI, m.p. 140–141° and 30 ml. of benzene was added 0.29 g. (0.0025 mole) of thionyl chloride and the mixture was stirred for 2 hr. The solution was heated at the reflux temperature for 15 min., cooled, and the white precipitate which formed was collected to give a quantitative yield of XI, m.p. 410–415° dec. The material was reprecipitated from a chloroform solution obtained by continuous extraction to give the analytical sample.

*Anal.* Calcd. for $(C_{12}H_8O_2)_n$: C, 78.25; H, 4.37. Found: C, 77.97; H, 5.10.

The infrared spectrum (Nujol mull) showed maxima at 1082 and 1067 cm.$^{-1}$ (C–O str.). The material was only slightly soluble in the common organic solvents. Due to low solubility of the material, a molecular weight could not be obtained.

(2) **With Acetyl Chloride.**—To a mixture of 0.500 g. (0.0025 mole) of VI, m.p. 106–107°, and 100 ml. of benzene was added 0.196 g. (0.0025 mole) of freshly distilled acetyl chloride. The mixture was stirred overnight during which time 0.37 g. of a white precipitate, m.p. 410–420° dec., was obtained. The infrared spectrum (Nujol mull) was identical to that of the material obtained from the thionyl chloride reaction.

(3) **By Heating.**—Three grams of VI, m.p. 106–107°, was heated to 225° and then extracted with a large volume of hot chloroform. The solution was filtered and the filtrate was cooled to give a white precipitate of XII, m.p. 410–420° dec. The infrared spectrum (Nujol mull) showed this to be identical to the material from the acetyl chloride and thionyl chloride reactions.

**Bis(1,8-naphthaldehydic acid)pseudoanhydride (XII).**—A solution of 0.50 g. (0.0025 mole) of dialdehyde VI, m.p. 140–141°, in 150 ml. of xylene was heated at the reflux temperature for 2 days after which time the xylene was removed under reduced pressure to give a yellow oil. The oil was extracted with ethyl acetate to leave white residue, m.p. 316–322°. Evaporation of the ethyl acetate to dryness gave only a yellow oil which became more viscous on standing.

The white residue from the ethyl acetate extraction was recrystallized from benzene to give 75 mg. (15.8%) of white cubic crystals, m.p. 318–319°, (lit.[19] m.p. 310–313°). The melting point of a mixture of this material and an authentic sample of XII was undepressed. The infrared spectrum (Nujol mull) showed maxima at 1740 (C═O str.) and a broad band at 945 cm.$^{-1}$ and also was identical to the spectrum of the authentic sample.

**1,8-Naphthalic Anhydride (X).**—A solution of 0.50 g. (0.0025 mole) of VI, m.p. 106–107°, in 150 ml. of xylene was heated at the reflux temperature for 3 days while a slow stream of air was passed through the solution. The solution was evaporated to a small volume and cooled to give light brown needles which were recrystallized from benzene to afford 0.35 g. (71.4%) of pure X, m.p. 268–269.5° subl. (lit.[20] m.p. 270°). The infrared spectrum (Nujol mull) showed maxima at 1759 and 1792 cm.$^{-1}$ (anhydride).

**1,8-Divinylnaphthalene (I).**—To 250 ml. of liquid ammonia, in an atmosphere of dry nitrogen, containing a small amount of anhydrous ferric chloride, was added 1.8 g. (0.078 mole) of sodium in small portions. The solution was allowed to stand for 30 min., then 26.6 g. (0.0744 mole) of triphenylmethylphosphonium bromide was added with stirring. The ammonia was evaporated and 1 l. of dry, peroxide-free ether was added. A solution of 5.0 g. (0.025 mole) of aldehyde VI, m.p. 133–138° dec., in 500 ml. of benzene was heated at the reflux temperature for 30 min. after which time the hot benzene solution was added to the refluxing ether solution of triphenylphosphinemethylene over a period of 15 min. The solution was heated at the reflux temperature for 15 min., filtered and the solvents were rapidly removed under reduced pressure. The red residue was chromatographed on 250 g. of Merck alumina with 400 ml. of a 1:1 mixture of carbon tetrachloride-pentane. The first ten fractions (approximately 30 ml. each) were evaporated to dryness under reduced pressure to give 3.14 g. (70.3%) of I, m.p. 40–46°. The material was recrystallized from methanol, sublimed under reduced pressure and recrystallized from pentane to give pure product, m.p. 47–47.5°.

*Anal.* Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.06; H, 6.80.

The infrared spectrum (carbon disulfide and carbon tetrachloride) showed maxima at 908, 988, and 1628 cm.$^{-1}$, characteristic of the vinyl groups.

When the reaction was repeated and the red residue distilled instead of chromatographed, a low yield of I could be obtained. The fraction boiling from 86–88° (0.75 mm.) was collected and recrystallized from pentane to give 0.10 g. (2.3%) of I, m.p. 45–47°.

**Polymerization of 1,8-Divinylnaphthalene (I) (Table I).** (1) **In Bulk.**—A mixture of 1.042 g. of I and 25 mg. of benzoyl peroxide was heated at 95° for 5 days in a sealed tube under nitrogen. The brittle glass which resulted was dissolved in benzene and precipitated by the addition of the benzene solution to methanol to yield 0.687 g. (65.9%) of poly(1,8-divinylnaphthalene) (XVIII). The infrared spectrum (carbon disulfide and carbon tetrachloride) showed no vinyl unsaturation. An analytical sample reprecipitated from benzene by methanol melted at 204°.

*Anal.* Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.12; H, 6.88.

(2) **In Emulsion.**—To 4 ml. of soap solution prepared from 0.05 g. of potassium persulfate, 0.05 g. of sodium hydrogen phosphate and 1.0 g. of saturated soap in 100 g. of water was added 2.0 g. of I. The mixture was sealed in a bottle in a nitrogen atmosphere and shaken at 70° for 15 hr., after which time the emulsion had broken. The polymer was coagulated with a 10% alum solution to afford 0.058 g. (2.9%) of polymer after one reprecipitation from benzene. The infrared spectrum of this polymer was identical to that obtained from polymerization in bulk. Only 0.4 g. of monomer could be recovered.

(3) **With a Titanium Tetrachloride-Aluminum Triisobutyl Catalyst.**—The catalyst was prepared by adding under nitrogen 0.62 ml. (0.25 mmole) of a 10% solution of aluminum triisobutyl in heptane to 0.21 ml. (0.08 mmole) of a 10% solution of titanium tetrachloride in heptane. To this catalyst was added a solution of 1 g. (5.55 mmoles) of I in 5.2 ml. of heptane, giving a molar ratio of catalyst to monomer of 0.6:1 and a solvent to monomer ratio of 6:1 by weight. The polymerization was carried out under nitrogen for 3 days after which time the reaction was terminated by the addition of methanol to yield 0.008 g. (0.8%) of XVIII.

When the polymerization was carried out using benzene as a solvent a 0.9% conversion to polymer was obtained.

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