

(The Tipp Manufacturing Co., Tipp City, Ohio). A slight vacuum was maintained by keeping the mercury leveling bulb a few centimeters below the mercury level in the gas buret. The evolved gases were collected in the liquid nitrogen trap. After cessation of gas evolution the source of heat was removed, mercury in the gas buret was raised to zero, gases in the reaction tube were pumped over to the trap, and the reaction tube was separated without letting air into the trap. With the pyrolytic products frozen in the liquid-nitrogen trap, the helium was removed by evacuating the system to 1 mm. The liquid nitrogen was then removed and the trap was warmed to allow the gases to expand into the gas buret where the volume of gas formed could be measured at ambient temperature and pressure. Percent yield of butenes then was calculated by converting the volume to STP and comparing with the theoretical volume based on sample weight.

Since the butenes vaporized from their frozen state at different rates, their ratios in the gas buret were not constant. Therefore, the gas were recollected in the trap by applying liquid nitrogen. When the gas volume was not much greater than the volume of the trap (frequently the case when the 160-ml. trap was used), the tubing at the entry and exit tubes were clamped and the trap was removed from the system. When the sample again vaporized, the gases were mixed by shaking with 1 ml. of mercury added prior to pyrolysis. When the volume was large in comparison with the 35-ml. trap, the gases were transferred to a 100-ml., round-bottomed flask fitted with side arm and stopcock and containing 1 ml. of mercury for mixing purposes. A T-tube was connected between the liquid nitrogen trap and the flask. The system was pumped down to 1 mm. and clamped at the T-joint. By cooling the flask in liquid nitrogen while the trap was warmed and opened to the flask, the gases collected in the flask. The flask was removed from the system and warmed to room temperature, and the gases were mixed by shaking with mercury (present in the flask before transfer). A hypodermic syringe was used to collect a sample of the gas for analysis by gas chromatography.

One small-scale (2 mmoles) pyrolysis of TBP was run in increments comprising approximately one-third of total decomposition. The gases collected from each portion were analyzed to determine the extent of isomerization in each stage.

Similarly, large-scale runs (50 to 90 mmoles) were made to determine the composition of the volatile liquids as a function of extent of TBP decomposition. The decomposition products were collected in a Dry Ice trap at 180–250 mm. in a closed system. The extent of decomposition was determined at intervals by stopping the pyrolysis and measuring the volume of gas formed.

Chromatography.—A Perkin-Elmer Model 154 vapor fractometer, equipped with a thermistor-type thermal conductivity detector, was used in the gas-liquid chromatographic analyses. Helium served as the carrier gas. A hypodermic syringe was used to inject the samples (up to 0.5 ml. of gas and up to 0.030 ml. of liquid).

Liquids were analyzed at 100–125° on a 1-m. column of 23 wt. % dinonylphthalate on 30–50-mesh celite. The carrier gas flow was 50 ml./min.

Gases were separated at 20–25° using a 13-ft. column of *o*-nitrophenetole¹⁷ at a flow rate of 50 ml. of helium per minute, or on a 12-ft. column of 29 wt. % of a 1:1 solution of silver nitrate in benzyl cyanide^{18,19} on 50–70-mesh celite at a flow rate of 35 ml. of helium per minute. The latter column readily separated the small amount of isobutylene from the main components, and although the butene-1 and *cis*-butene-2 came off as one peak the percentage of isobutylene in the mixture could be easily determined. When a ratio of one weight of silver nitrate to three weights of benzyl cyanide, close to the literature value,¹⁹ was used on 30–50-mesh celite in a 16-ft. column, *trans*-butene-2, butene-1, and *cis*-butene-2 were separated in that order but the small amount of isobutylene present was masked by the large *trans*-butene-2 peak. Ethyl alcohol (50%) was used as the solvent for the silver nitrate-benzyl cyanide solution used in the preparation of the celite column packing. The solvent was removed in the dark at reduced pressure. The dried material was rescreened and packed in 0.25-in. copper tubing 12 ft. in length. The column was coiled to fit in the gas chromatograph.

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Coupling of Naphthalene Nuclei by Lewis Acid Catalyst-Oxidant¹

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Naphthalene reacted readily under mild conditions in *o*-dichlorobenzene with ferric chloride-water, aluminum chloride-cupric chloride, and molybdenum pentachloride. With ferric chloride-water, 1,1'-binaphthyl and 1,4-di- α -naphthyl-naphthalene comprised the isolable hydrocarbons. In the case of molybdenum pentachloride and aluminum chloride-cupric chloride, the binaphthyl fraction consisted of an isomeric mixture in which the 2,2' form predominated. Molecular weight data on the crude products indicated an average of about 3–6 naphthalene units per chain. An oxidative cationic mechanism is proposed for the coupling reactions. Apparently the polymerization proceeds *via* coupling in the 1 and 4 positions of the naphthalene monomer. The initially formed products are then subsequently isomerized in those systems containing sufficiently active catalyst.

It was recently shown that aromatic nuclei can be coupled under mild conditions by exposure to Lewis acid catalyst-oxidant, such as ferric chloride,² molybdenum pentachloride,³ or aluminum chloride-cupric chloride.⁴ With benzene as the monomer, *p*-polyphenyl was obtained in almost quantitative yield.⁵ *p*-Sexi-phenyl proved to be the principal product which resulted from either biphenyl or *p*-terphenyl.⁶ Studies

with ferric chloride revealed the formation of bimesityl from mesitylene,⁷ and bixylyls from *m*- and *p*-xylene.^{8,9}

Our objective was to investigate the behavior of naphthalene in the system, Lewis acid catalyst-oxidant, and to obtain information concerning the mechanistic aspects. In an earlier paper, brief mention was made of the 1-chloronaphthalene-ferric chloride reaction which yielded a dichlorobinaphthyl (not completely characterized).¹⁰ Before 1900 several investigators reported 1,1'-binaphthyl as a component of the tarry product formed by interaction of naphthalene with

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(3) P. Kovacic and R. M. Lange, *ibid.*, **28**, 968 (1963).

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(5) P. Kovacic and J. Oziomek, *J. Org. Chem.*, **29**, 100 (1964).

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TABLE I
 NAPHTHALENE-FERRIC CHLORIDE^a

H ₂ O- FeCl ₃ , M	C ₁₀ H ₈ - FeCl ₃ , M	Temp., °C.	Time, hr.	Crude product				1,1'-Bi- naphthyl, %	1,1'-Bi- naphthyl, % yield
				Wt., g.	Av. mol. wt. ^b	C/(H + Cl) ^c	Cl, %		
0	2	20-25	2	0.4	24	1
0	2	20-25	12	2.4	520 ^d	1.63	6.25	10	3
0.25	2	20-25	2	2.8	19	3
0.5	2	20-25	2	3.6	16	7
1 ^e	2	-15	2	0.85	400	1.55	1.76	27	3
1 ^f	2	0-3	9	3.8	520	1.54	3.96	12	6
1	0.5	20-25	2	3	560 ^d	9	3
1	1	20-25	2	3.7	520	12	5
1	2	20-25	2	4	500	1.53	1.68	21	11
1	8	20-25	2	3.7	21	10
1 ^g	2	20-25	2	3.9	380	26	13
1 ^h	2	20-25	2	4	420	16	7
1	2	70-80	0.17	3.2	440 ^d	1.59	8.38	9	3
2	2	20-25	2	3.4	410	1.48	1.47	28	12
2	2	20-25	4	3.8	31	15
2	2	40-45	2	3.4	26	12
4	2	20-25	2	0.6	...	1.30	2.93	5	1.5
6	2	20-25	2	0

^a Ferric chloride (0.0625 mole), *o*-dichlorobenzene (0.75 mole). ^b 75-85% benzene soluble. ^c Calculated C/H values: naphthalene, 1.25; binaphthyl, 1.43; ternaphthyl, 1.49; quaternaphthyl, 1.54; polynaphthyl, 1.67. The polymers were analyzed for carbon, hydrogen, and chlorine. ^d About 60% soluble. ^e Chlorobenzene solvent (0.75 mole). ^f Scale 20X. ^g Carbon disulfide solvent (0.75 mole). ^h 1,2,4-Trichlorobenzene solvent (0.75 mole).

manganese dioxide in sulfuric acid.^{11,12} Most of the references dealing with the effect of aluminum halides on naphthalene are found in the early literature.¹³ Among the products obtained were 2,2'-binaphthyl, alkynaphthalenes, hydronaphthalenes, perylene, and polymers.^{13,14}

Results and Discussion

Naphthalene reacted readily under mild conditions in *o*-dichlorobenzene with ferric chloride^{14a}-water, aluminum chloride-cupric chloride, and molybdenum pentachloride. The organic products included binaphthyls, ternaphthyl, and higher molecular weight material.

With ferric chloride-water, 1,1'-binaphthyl and 1,4-di- α -naphthyl-naphthalene comprised the isolable hydrocarbons arising *via* nuclear coupling (Table I). There was no evidence for the presence of the other isomeric binaphthyls. 1,1'-Binaphthyl, which represented 5-31% of the crude product could be separated in about 15% yield based on the metal halide.²⁻⁴ Since uncomplicated techniques are involved, this provides a convenient, one-step synthesis of the "dimer." Previous preparative procedures include coupling of 1-halonaphthalenes by the Ullmann, Fittig, or Grignard methods.^{12,15,16} From a first-hand comparison, we rate ferric chloride superior to manganese dioxide-sulfuric acid^{11,12} for effecting this transformation.

In addition, there is now available for the first time a simple route for the preparation of 1,4-di- α -naphthyl-

naphthalene in small quantities. In 1962 the synthesis of this hydrocarbon was disclosed by Buchta and Boesche¹⁷ who used an eleven-step sequence based on 1-chloro-1,2,3,4-tetrahydronaphthalene.

In the case of aluminum chloride-cupric chloride, the binaphthyl fraction consisted of an isomeric mixture in which the 2,2' form predominated (Table II). Molybdenum pentachloride gave similar results except for somewhat lower yields (Table III). The isomeric binaphthyls were identified by comparison of their v.p.c. retention times, melting points, infrared spectra, and ultraviolet spectra with those of the authentic materials. The literature contains numerous references to 2,2'-binaphthyl as a product arising from exposure of naphthalene to high temperatures.¹⁸

Molecular weight determinations were carried out on the benzene-soluble fractions (usually >75%) of the crude products formed by means of the various metal halides (Tables I-III). The data indicate an average of 3-6 naphthalene units per chain, pointing to a high proclivity for termination.

There was generally good agreement between the C/(H + Cl) atomic ratios and the molecular weight values based on a completely aromatic structure for the products from ferric chloride and molybdenum pentachloride. However, with aluminum chloride-cupric chloride low ratios were obtained pointing to the presence of partially reduced nuclei. This is not surprising since in most cases more product was formed than would be expected from the amount of cupric chloride present. With ferric chloride and molybdenum pentachloride less than the theoretical yield of product was produced. Dehydrogenation studies were carried out with the aluminum chloride-cupric chloride produced polymer at about 300° with palladium on

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TABLE II
NAPHTHALENE-ALUMINUM CHLORIDE-CUPRIC CHLORIDE

AlCl ₃ - CuCl ₂ , M ^a	Temp., °C.	Time, hr.	Wt., g.	Av. mol. wt. ^b	Crude product			Binaph- thyl, %	Binaphthyl, % yield		
					C/(H + Cl)	Cl, %			1,1'	1,2'	2,2'
0.1	20-25	2	2	35	14	43	43	
1	20-25	2	8.2	490	1.39	0.94	14	20	15	65	
2	20-25	2	10	18	31	14	55	
1	20-25	0.5	6.8	420	1.36	0.82	12	32	13	55	
1	20-25	9	7.4	480	1.36	0.46	4	0	19	81	
1 ^c	-15	2	0.7	345	1.32	2.22	35	18	20	62	
1 ^c	0-3	10	6.3	480	1.38	1.49	32	7	12	81	
1	75-80	0.17	6.7	465 ^d	12	39	20	41	
1 ^e	55-60	3	5.1	11	32	9	59	
1 ^f	20-25	2	2.4	8	0	7	93	
∞ ^g	20-25	2	1.8 ^h	
0 ⁱ	20-25	2	0	

^a Cupric chloride held constant at 0.0625 mole. ^b 90-100% benzene soluble. ^c Chlorobenzene (0.75 mole) solvent. ^d 82% soluble. ^e Nitrobenzene solvent. ^f Cuprous chloride (0.125 mole). ^g Aluminum chloride (0.0625 mole). ^h Very complex mixture. ⁱ Cupric chloride (0.0625 mole).

TABLE III
NAPHTHALENE-MOLYBDENUM PENTACHLORIDE^{a,b}

Temp., °C.	Crude product					Binaphthyl, % yield		
	Wt., g.	Av. mol. wt. ^c	C/(H + Cl)	Cl, %	Binaph- thyl, %	1,1'	1,2'	2,2'
-15	4.2	500	1.62	4.36	1.2	0	0	100
0-3	6.1	520	1.55	6.13	6.2	16	8	76
20-25	6.6	790	1.54	5.38	3.7	12	17	71
20-25 ^d	5.9	570	4	0	5	95

^a Time, 2 hr. ^b Chlorobenzene solvent. ^c 70-80% benzene soluble. ^d *o*-Dichlorobenzene solvent.

carbon, conditions which are known to effect complete aromatization of partially hydrogenated naphthalenes.^{17,19} A decrease in the hydrogen content confirmed the presence of some reduced structures. N.m.r. investigations showed a pronounced reduction in the weak band at 3.3 p.p.m. (aliphatic protons) after the palladium treatment. For the other original polymers there was no distinct evidence in the n.m.r. spectra for the presence of aliphatic protons. The spectrum of the ferric chloride produced product was essentially unchanged following exposure of the polymer to palladium. For the various products a complex series of strong bands was present in the region, 7.2-8.2 p.p.m. (aromatic protons).

With aluminum chloride-cupric chloride, product yield and composition were dependent upon the amount of catalyst present. Binaphthyl yield attained a maximum after about 1.5 hr. and then decreased (Table IV).

The molecular weight of the product varied with change in the naphthalene-ferric chloride ratio in certain regions. 1,2,4-Trichlorobenzene and carbon disulfide also functioned satisfactorily as solvents. Attention was devoted to the temperature and time variables. At low temperatures molybdenum pentachloride proved to be the most effective agent for coupling.

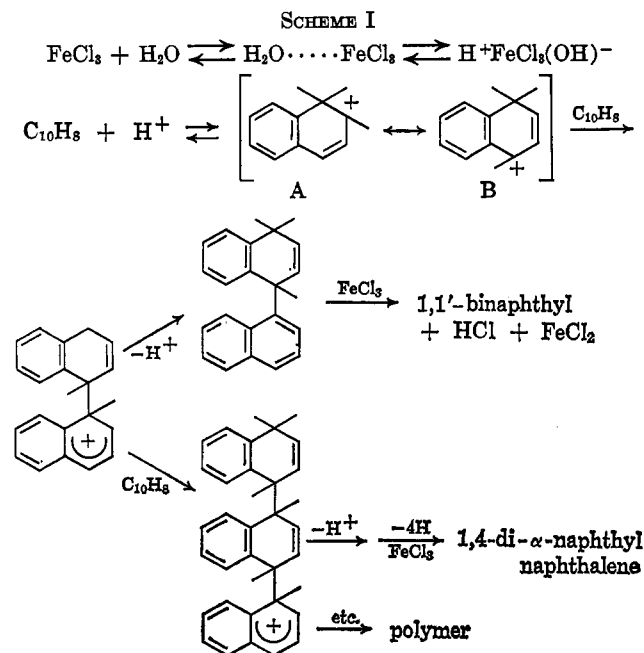
Only small amounts of chlorinated material were present in the naphthalene product mixtures. In contrast, alkyl- and halobenzenes are known to undergo nuclear chlorination to major extents with ferric chloride.^{10,20}

TABLE IV
BINAPHTHYL YIELD vs. TIME^a

Time, min.	Binaphthyl, relative yields
10	1
30	1.4
50	1.6
70	1.9
100	2.1
130	2.0
190	1.8
250	1.5
430	1.2

^a C₁₀H₈, 0.125 mole; AlCl₃, 0.00625 mole; CuCl₂, 0.0625 mole; *o*-C₆H₄Cl₂, 0.75 mole.

For the coupling reactions with metal halides, we propose an oxidative cationic mechanism (Scheme I) similar to that advanced previously for analogous transformations involving benzene,⁴ biphenyl,⁶ *p*-



(19) R. P. Linstead, *et al.*, *J. Chem. Soc.*, 1146 (1937); C. D. Nenitzescu and M. Avram, *J. Am. Chem. Soc.*, **72**, 3486 (1950).

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terphenyl,⁶ and α -naphthyl ethyl ether.²¹ The end result points to the involvement of form B rather than A in the propagation phase.

The formation of comparatively low molecular weight products relates naphthalene to biphenyl,⁶ *p*-terphenyl,⁶ and mesitylene,⁷ rather than to benzene.⁴ It appears that the highest degree of polymerization is associated with the most active propagating species, *i.e.*, the carbonium ion possessing the least delocalization.

Our data indicate that 1,1'-binaphthyl, which is probably formed initially in all cases, is subsequently isomerized in those systems containing sufficiently active Lewis acid catalysts, namely, aluminum chloride and molybdenum pentachloride (Tables II and V).

TABLE V
ISOMERIZATION OF 1,1'-BINAPHTHYL

Agent	Time, hr.	Binaphthyl, %			Bi-naphthyl present, %
		1,1'	1,2'	2,2'	
AlCl ₃	1	34	18	48	...
	2	5	9	86	80
AlCl ₃ -CuCl	1	64	26	10	99
	2	49	25	27	99
AlCl ₃ -HCl	0.08	2	10	88	...
MoCl ₅	0.08	36	30	34	94
	1	35	24	41	76
MoCl ₅ -HCl	2	28	26	46	74
	0.08	8	5	88	58
FeCl ₃	1	0	4	96	38
	2	0	4	96	34
FeCl ₃	2	100	100
FeCl ₃ ·H ₂ O	168	100	100

The mechanistic aspects of this type of rearrangement have been discussed by previous investigators.^{22,23} Isomerization studies were carried out with the individual binaphthyls in contact with the metal halide catalyst at 20–25°. Neither 1,1'- nor 2,2'-binaphthyl was rearranged on exposure to ferric chloride (anhydrous or hydrated). On the other hand, aluminum chloride and molybdenum pentachloride converted 1,1'-binaphthyl to the 2,2' isomer *via* the 1,2' intermediate. Weitzenböck had previously effected the transformation of 1,1'-binaphthyl to the 2,2' structure by exposure to aluminum chloride.²⁴ The rate of isomerization of 1,1'-binaphthyl was accelerated by the addition of hydrogen chloride, pointing to a co-catalytic effect. Cuprous chloride acted as an inhibitor. Treatment of 2,2'-binaphthyl with aluminum chloride produced only the 1,2' form in low conversion, presumably in an equilibrium situation. Apparently, thermodynamic stability²⁵ is a driving force of consequence in the isomerization.

In related work, each of the terphenyls was transformed to an equilibrium mixture of 63% *m*- and 35% *p*-terphenyl under the influence of aluminum chloride.²⁶ More recently, Wynberg and Wolf²² showed that in the

presence of this catalyst diphenyl-1,1'-C¹⁴ undergoes random distribution of the C¹⁴. Similarly, 1-phenyl-naphthalene is rearranged to the 2 isomer on exposure to acid catalysts.²⁷

Orientation in naphthalene alkylation is also critically dependent upon the nature and amount of the catalyst.^{28a} With aluminum chloride catalyst, butyl chloride or benzyl chloride gave rise to the 2 isomer principally. On the other hand, a weaker catalyst resulted mainly in 1 substitution.^{28b}

Failure of ferric chloride hydrate to convert 1,1'-binaphthyl to higher molecular weight material demonstrates that this hydrocarbon is not an intermediate in the naphthalene propagation sequence. On the other hand, binaphthyl was transformed to other products on exposure to aluminum chloride or molybdenum pentachloride (Table V).

In the initiation and propagation phases of the nuclear coupling, aluminum chloride is designated the catalyst and cupric chloride the oxidant. Ferric chloride and molybdenum pentachloride can presumably function in a dual capacity. When aluminum chloride was omitted, failure of reaction to occur attested to the critical role of the catalyst. In the absence of cupric chloride, there was a drastic decrease in the yield of crude product. Support for the dehydrogenation phase of our hypothesis is provided by the facility with which ferric chloride,² molybdenum pentachloride,³ and cupric chloride²⁹ convert dihydrobenzene structures to the corresponding aromatized form. The reported isolation of 2,2'-binaphthyl and hydronaphthalenes from naphthalene-aluminum chloride reaction mixtures subjected to more drastic conditions indicates that disproportionation occurs when a suitable oxidant is not present.¹³

The strength of the Lewis acid catalyst is a crucial factor. For example, no reaction occurred in the naphthalene-cupric chloride system on addition of the relatively weak Friedel-Crafts halides, stannic chloride, and titanium tetrachloride. Also, in the presence of nitrobenzene a higher reaction temperature was required indicating a decrease in catalyst potency through coordination with solvent (Table II). Addition of a large amount of cuprous chloride to naphthalene-aluminum chloride-cupric chloride resulted in a marked decrease in yield. This inhibitory effect, also noted in 1,1'-binaphthyl isomerization, benzene polymerization,⁵ and coupling of biphenyl nuclei,⁶ can be attributed to deactivation of the catalyst by inclusion in a ternary complex.^{5,30} Thus, it appears that catalyst potency has an important bearing on initiation and isomerization, and perhaps on dehydrogenation.⁵ One can conclude from the data that molybdenum pentachloride has greater catalytic activity than ferric chloride.

In the ferric chloride systems, the effect of variation in water concentration provided evidence for cocatalysis by Brønsted acid (Table I). The yield of crude product attained a maximum at a water-ferric chloride molar ratio of 1, similar to the findings in the benzene

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(30) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **85**, 4046 (1963).

reaction.³¹ Whereas there was essentially no polymerization with benzene at a 2:1 ratio, or with no added water, appreciable reaction occurred in the case of naphthalene. The greater reactivity of naphthalene permits the use of a less active catalyst-cocatalyst complex or trace amounts of the most effective complex.³² In previous work, polymer yield from benzene-aluminum chloride-cupric chloride varied inversely with the amount of added water.⁵ Evidence has been presented for cocatalysis by hydrogen bromide in the naphthalene-aluminum bromide reaction.¹⁴ Hydrogen chloride exerted no cocatalytic effect in the benzene-ferric chloride reaction.³³ In a recent study of hydrogen chloride cocatalysis in the cationic polymerization of propylene, the highest activity was observed with an aluminum chloride-hydrogen chloride ratio of 1.³⁴

Mechanistically, a similar scheme involving nuclear coupling of form B and subsequent rearrangement has been invoked to rationalize the formation of 2,2'-binaphthyl and polymer from decarbonylation of 1,4-dihydro-1-naphthoyl chloride in the presence of aluminum chloride.³⁵ The possible existence of other intermediates, *e.g.*, π complexes, during the naphthalene reactions should also be considered. Recently, on the basis of spectral evidence, Perkampus and Kranz proposed σ -complex formation from naphthalene and aluminum chloride.³⁶ Electron spin resonance investigations point to the presence of organic radical cations in systems containing polynuclear hydrocarbons and certain Lewis acids.³⁷⁻³⁹

Any theoretical treatment should take into account the heterogeneous nature of the reaction mixtures. The investigated metal halides possess relatively low solubility in these systems.

Experimental⁴⁰

Materials.—Naphthalene, 1,1'-binaphthyl, 2-bromonaphthalene, α -tetralone, and nitrobenzene were obtained from Eastman; aluminum chloride, cupric chloride, and cuprous chloride from Fisher; 2,2'-binaphthyl from Gallard-Schlesinger; anhydrous ferric chloride, sublimed powder, from Matheson Coleman and Bell; and anhydrous molybdenum pentachloride from Climax Molybdenum Co. *o*-Dichlorobenzene (Sargent) and chlorobenzene (Eastman) were distilled from calcium hydride.

Anhydrous ferrous chloride was prepared from anhydrous ferric chloride and chlorobenzene.⁴¹ 1,2'-Binaphthyl was synthesized from 2-bromonaphthalene and α -tetralone according to the method of Hooker and Fieser.⁴²

Naphthalene-Ferric Chloride. General Procedure.—The reactions were run in a 250-ml., three-neck flask fitted with a paddle stirrer, thermometer, and gas inlet and outlet tubes. In the reaction with anhydrous ferric chloride, the metal halide was weighed directly into the flamed reaction flask in a drybox,

and the naphthalene-*o*-dichlorobenzene solution was dried over phosphorus pentoxide. Addition of water to the mixture of ferric chloride, naphthalene, and *o*-dichlorobenzene was made with cooling and efficient stirring. Ferric chloride hexahydrate was used in the form of the commercial product.

After 2 hr. at the desired temperature, the black reaction mixture was added to 1 l. of 6 *N* hydrochloric acid. The mixture was then steam distilled to remove the *o*-dichlorobenzene and unchanged naphthalene. The solid organic residue was dissolved in *o*-dichlorobenzene, and the resulting solution was extracted with 6 *N* hydrochloric acid until the aqueous phase became colorless. After the organic solution was exhaustively steam distilled, the residue was powdered with ice-water in a blender, filtered, and dried. The yield and isomer distribution of the binaphthyls were determined by dissolving 0.1 g. of the crude product in benzene containing a known amount of *m*-terphenyl as an internal standard for gas chromatographic analysis (6 ft. \times 0.25 in. column, 10% silicone grease on Chromosorb W at 215°). The results are listed in Table I.

In several cases the reaction product was sublimed in a 100 \times 2 cm. vertical tube at 0.2–0.3 mm. The volatile components separated in zones, principally two distinct bands in the cooler portions of the apparatus. Gas chromatography showed that the first band consisted primarily of the binaphthyl fraction, and the second one contained predominantly ternaphthyl. The results are in agreement with those obtained by gas chromatography.

Repeated sublimation of the ternaphthyl fraction, obtained from the $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ reaction at 0° for 9 hr., yielded white crystals of 1,4-di- α -naphthyl-naphthalene, m.p. 191.5–192.5, m.m.p. 191–192°, lit.³⁷ m.p. 193–194°. The ultraviolet spectrum ($\lambda_{\text{max}}^{\text{C}_6\text{H}_6}$ 298 m μ) and infrared spectrum (carbon disulfide solvent, strong, 7.26, 12.52, 12.85, 12.90, 13.11 μ ; weak, 3.27, 11.83 μ) were identical with those of the authentic material.⁴³ There was also present a dark red, less volatile component, m.p. 210–214°, which was not characterized. The corresponding fraction from the naphthalene-aluminum chloride-cupric chloride reaction was shown by gas chromatography to contain at least seven components.

Naphthalene-Aluminum Chloride-Cupric Chloride.—The general procedure was used with slight modifications. Cupric chloride (18.4 g., 0.0625 mole) and then aluminum chloride (8.3 g., 0.0625 mole unless otherwise noted) were added to a solution of naphthalene (16 g., 0.125 mole) in *o*-dichlorobenzene (110 g., 0.75 mole). The results are listed in Table II. Perhaps some aromatization of reduced forms occurred during gas chromatography or sublimation in the work-up procedure.

Naphthalene-Molybdenum Pentachloride.—The general procedure was followed. The data are tabulated in Table III.

Naphthalene-Metal Halides. Binaphthyl Yield vs. Time.—The general procedure was followed at 20–25°. Samples (0.2 ml.) were removed with an eye dropper for determination of binaphthyl yield by v.p.c. analyses. Data for $\text{AlCl}_3\text{-CuCl}_2$ are given in Table IV. With molybdenum pentachloride the concentration of binaphthyls reached a maximum after a few minutes and then slowly decreased. With $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ the 1,1'-binaphthyl concentration reached a maximum in about 1 to 2 hr. and then decreased very slowly.

Naphthalene-2,2'-Binaphthyl-Ferric Chloride.—Naphthalene (0.125 mole) was allowed to react at 20–25° with $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ (0.0625 mole of each) in *o*-dichlorobenzene (0.75 mole) in the presence of 2,2'-binaphthyl (0.0039 mole) according to the general procedure. Several samples were removed during 2 hr. and analyzed by gas chromatography. The 2,2'-binaphthyl concentration steadily decreased while that of 1,1'-binaphthyl increased during the reaction period. No 1,2'-binaphthyl was detected.

Dehydrogenation of the Naphthalene-Aluminum Chloride-Cupric Chloride Product.—The reaction (5 \times scale) was carried out in *o*-dichlorobenzene with $\text{AlCl}_3\text{-CuCl}_2$ (1:1) at 20–25° for 2 hr. Exposure of the product to *o*-dichlorobenzene at room temperature effected separation into soluble (28 g.) and insoluble (0.5 g.) fractions. The soluble polymer (25 g.), C/(H + Cl) = 1.34, was heated with 5 g. of 5% palladium on carbon for 2 hr. at 315 \pm 10° under nitrogen. Extraction of the reaction mixture at 80°, first with benzene and then with *o*-dichlorobenzene, gave 23.5 g. of product, C/(H + Cl) = 1.44.

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