

preparation of twenty-three varied vinyl aromatic compounds, of which the following have not been previously reported: *m*-ethylstyrene, 3,5-diethylstyrene, *p*-*t*-butylstyrene, *p*-cyclohexylstyrene, 6-vinyl-1,2,3,4-tetrahydronaphthalene, *p*-phenoxy-styrene, 1-chloro-4-vinylnaphthalene, 2-vinylfluorene, 1-vinylnaphthalene, 2-vinyldiphenylene oxide and 4-chloro-4'-vinylbiphenyl.

The intermediate carbinols from which these eleven compounds were prepared are characterized and their preparation from the analogous arylmethyl ketones is described. The Perrier modification of the Friedel-Crafts synthesis is shown to be especially advantageous for the acetylation of alkylbenzenes and thiophene.

DAYTON, OHIO

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[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, MONSANTO CHEMICAL CO.]

## Vinyl Aromatic Compounds. II. o-, m- and p-Vinylbiphenyls

BY W. FREDERICK HUBER, MARY RENOLL,<sup>1</sup> ALFRED G. ROSSOW AND DAVID T. MOWRY

The vapor-phase dehydration of arylmethylcarbinols<sup>2</sup> to the analogous vinyl aromatic compounds has been extended to the preparation of all three isomers of vinylbiphenyl. *o*-Vinylbiphenyl has been synthesized by Bradsher and Wert,<sup>3</sup> who obtained a 24% yield by conducting the dehydration of *o*-biphenylmethylcarbinol in the liquid phase over potassium bisulfate at 160°. By the vapor phase dehydration we have obtained a 70% yield of *o*-vinylbiphenyl.

*p*-Acetylbiphenyl has been prepared by the action of acetic acid on biphenyl in liquid hydrogen fluoride solution in 45% conversion and 70% yield.

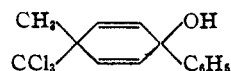
*p*-Biphenylmethylcarbinol, m. p. 97°, was prepared by catalytic hydrogenation of *p*-phenylacetophenone. This carbinol has been previously made by Adam<sup>4</sup> who reduced the ketone with sodium and alcohol and reported a melting point of 85–86°. It was our experience that when ethanol was used as a solvent for recrystallization the melting point could not be raised above 86°, but when a mixture of benzene and ligroin was used the purer material of m. p. 97° was easily obtained. Vapor phase dehydration of the carbinol gave 75–85% yields of *p*-vinylbiphenyl.

*m*-Vinylbiphenyl was prepared according to the synthesis outlined. The synthesis for *m*-bromobiphenyl in 51% over-all yield from readily

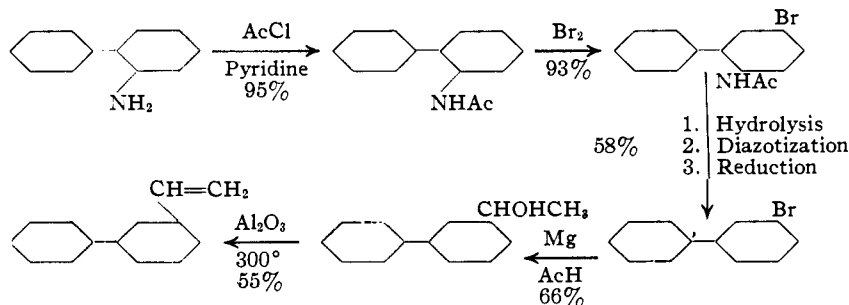
available *o*-aminobiphenyl represents an improvement over the known<sup>5</sup> somewhat hazardous method of coupling *m*-bromobenzenediazonium hydroxide with benzene in 28%<sup>6</sup> yield.

In order to obtain comparative descriptive data the previously unreported *o*- and *m*-acetylbiphenyls and the *o*- and *m*-ethylbiphenyls were prepared.

*p*-Ethylbiphenyl also was synthesized by catalytic hydrogenation of *p*-biphenylmethylcarbinol and melted, after repeated recrystallization from methanol, at 34.0–34.5°. Auwers and Julicher<sup>7</sup> have reported this compound to melt at 46–47°. Their compound originated from the formic acid dehydration and vacuum distillation of the compound



and it was stated to be identical with a sample prepared by the Clemmensen reduction of *p*-acetylbiphenyl. In order to clarify this discrepancy, *p*-ethylbiphenyl was synthesized by two more independent methods, *i.e.*, the Clemmensen reduction of *p*-acetylbiphenyl and by the repeated low-temperature recrystallization of the mixture of *m*- and *p*-ethylbiphenyls obtained by ethylation of biphenyl. Both samples melted at 34.0–34.5°, and were identical with the original sample. We have concluded, therefore, that the earlier work is in error. Since the ultimate analysis reported by Auwers and Julicher for their degradation product conforms to that required by *p*-methylbiphenyl almost as closely as to that required by *p*-ethylbiphenyl and, since the former compound is known<sup>8</sup> to melt at 47–48°, it is possible that the com-



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(2) Mowry, Renoll and Huber, *THIS JOURNAL*, **68**, 1105 (1946).

(3) Bradsher and Wert, *ibid.*, **62**, 2806 (1940).

(4) Adam, *Bull. soc. chim.*, [2] **49**, 97–102 (1888).

(5) Gomberg and Bachmann, *THIS JOURNAL*, **46**, 2339 (1924).

(6) Marvel, Ginsberg and Mueller, *ibid.*, **61**, 77 (1939), report 16% yields.

(7) Auwers and Julicher, *Ber.*, **55B**, 2167 (1922).

(8) Gattermann, *Ann.*, **347**, 381 (1906).

TABLE I  
BIPHENYL DERIVATIVES

Compound	Yield, %	B. p., °C.		M. p., °C.	$n_D^{20}$	Un- satn., <sup>a</sup> %	Analyses, <sup>i</sup> %			
		°C.	mm.				Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found
<i>o</i> -Ethylbiphenyl	97	128-129	11	-6	1.5758	..	92.26	92.23	7.74	7.97
<i>m</i> -Ethylbiphenyl	40	143	11	.. <sup>b</sup>	1.5876	..	92.26	92.07	7.74	7.86
<i>p</i> -Ethylbiphenyl	98	146-147	11	34 <sup>b</sup>	1.5891 <sup>b</sup>	..	92.26	92.34	7.74	7.96
<i>o</i> -Acetylbiphenyl	88	158	11	56	..	..	85.68	85.86	6.16	6.20
<i>m</i> -Acetylbiphenyl <sup>c</sup>	81	137-138	1	.. <sup>c</sup>	1.6142	..	85.68	85.53	6.16	6.14
<i>p</i> -Acetylbiphenyl	70	168	6	121	..	..	..	..	..	..
<i>o</i> -Biphenylmethylcarbinol <sup>c</sup>	79	..	..	111-112	..	..	..	..	..	..
<i>m</i> -Biphenylmethylcarbinol	66	146-149	1	.. <sup>c</sup>	1.6098	..	84.81	84.76	7.12	7.00
<i>p</i> -Biphenylmethylcarbinol <sup>d</sup>	90	..	..	97	..	..	84.81	84.81	7.12	7.06
<i>o</i> -Vinylbiphenyl <sup>d</sup>	70	114-117	1	.. <sup>e</sup>	1.6168	93.6	..	..	..	..
<i>m</i> -Vinylbiphenyl	55	112	1	.. <sup>e</sup>	1.6263	94.6	93.29	93.27	6.71	6.77
<i>p</i> -Vinylbiphenyl <sup>f</sup>	82	136-138	6	119	..	99.9	93.29	93.28	6.71	6.74

<sup>a</sup> By bromide-bromate titration, see Mulliken and Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 59 (1935). Very pure (99.6%) styrene gives values of 98-99% by this method. <sup>b</sup> Auwers and Julicher, ref. 7, report m. p. 46-47°. <sup>c</sup> Bradsher and Wert, ref. 3, report 56% yield, m. p. 110.5-111.5°. <sup>d</sup> Bradsher and Wert, ref. 3, report a 24% yield, b. p. 127-130° (5 mm.). <sup>e</sup> Solidified to a glass when cooled with Dry Ice. <sup>f</sup> Dr. John Mann Butler, private communication, has reported the first synthesis of this compound, m. p. 113-115° for a sample obtained in about 30% yield by the Tschugaeff dehydration of the carbinol. <sup>g</sup> This sample contained 97.2% ketone, see Bryant and Smith, *THIS JOURNAL*, **57**, 57 (1935). <sup>h</sup> At 35°. <sup>i</sup> Adam, ref. 10, reported m. p. 85-86°. <sup>j</sup> Microanalyses by the Arlington Laboratories, Fairfax, Virginia.

pound they obtained was *p*-methylbiphenyl. No explanation can be offered, however, for their results of the Clemmensen reduction of *p*-acetylbiphenyl which we were unable to duplicate.

The complete series of the isomers of acetylbiphenyl, ethylbiphenyl, biphenylmethylcarbinol and vinylbiphenyl are described in Table I.

### Experimental

***p*-Acetylbiphenyl.**—The acetylation of biphenyl with acetic acid in anhydrous hydrogen fluoride solution did not occur to an appreciable extent at room temperature or at higher temperatures in a static autoclave because of the low solubility of biphenyl in the solvent phase. Several runs were made in a 500-cc. stainless steel autoclave equipped with an 1800 r. p. m. stirrer. One fourth mole of biphenyl, 0.25 mole of acetic acid and 200 g. of anhydrous hydrogen fluoride were charged to the autoclave, heated for three and one-half hours, cooled and decanted into water. Unreacted biphenyl being insoluble was recovered from the autoclave. The product was filtered from the water solution, dried and distilled to give nearly pure, colorless *p*-acetylbiphenyl, b. p. 148-150° (2 mm.), and a small residue consisting chiefly of 4,4'-diacetylbiphenyl and resinous by-products. The monoketone was identical with a sample of *p*-acetylbiphenyl obtained from Eastman Kodak Co., m. p. 120-121°. Results from four typical runs are:

Temp., °C.	Pres- sure, p. s. i.	Biphenyl recov., %	<i>p</i> -Acetylbiphenyl		
			Conver- sion, %	Yield, %	Residue, %
80	85	..	14.9	..	0.8
90	100	61.2	25.9	67.5	12.4
100	130	35.3	45.0	70.3	16.8
110	170	19.0	31.6	39.5	48.2

Although approximately 85% of the hydrogen fluoride could be recovered in an essentially anhydrous condition by distilling it from the autoclave, a run at 100° in which only 25 g. of hydrogen fluoride was charged gave less than 2% conversion. Increasing the quantity of solvent from 200 to 300 g. gave only a slight improvement in conversion and yield.

***p*-Biphenylmethylcarbinol.**—*p*-Acetylbiphenyl was mixed with an equal weight of anhydrous ethanol, 4% by

weight of copper chromite catalyst<sup>9</sup> added and hydrogenated at 125-135° and 1200 lb. pressure in an American Instrument Co. rocking autoclave. The product, which could be recrystallized repeatedly from dilute ethanol without raising the melting point above 86°, was easily freed of contaminating *p*-ethylbiphenyl by recrystallization from a mixture of benzene and hexane. Yields of 80-90% of pure *p*-biphenylmethylcarbinol, m. p. 97° were obtained. Adam,<sup>10</sup> who conducted the reduction by the sodium-alcohol technique, reported m. p. 85-86°.

***p*-Vinylbiphenyl.**—The carbinol was dissolved in two parts of dioxane and dehydrated as previously described<sup>2</sup> over alumina at 310-320° and 30-40 mm. pressure. Distillation of the product using sulfur as an inhibitor gave an 82% yield of solid distillate, b. p. 136-138° (6 mm.), which recrystallized from ethanol in lustrous white plates, m. p. 119.0-119.5°.

***p*-Ethylbiphenyl.**—*p*-Biphenylmethylcarbinol was catalytically hydrogenated at 200° and 2000 p. s. i. with copper chromite catalyst to give an almost quantitative yield of *p*-ethylbiphenyl, b. p. 146-147.5° (11 mm.), m. p. 34.0-34.5°,  $n_D^{20}$  1.5891. Repeated recrystallization from methanol failed to raise the melting point.

Since the recorded<sup>7</sup> melting point of this compound was 46-47°, an independent synthesis of *p*-ethylbiphenyl from *p*-acetylbiphenyl was carried out by the Clemmensen reduction. Fifteen grams of *p*-acetylbiphenyl, m. p. 121°, was added to 70 g. of amalgamated zinc (prepared by shaking mossy zinc with acidified mercuric chloride solution in the usual manner) and 400 cc. of 1:1 hydrochloric acid and the solution was refluxed. Three additional 50-cc. portions of hydrochloric acid were added during the twenty-hour period of refluxing. Upon cooling, the oil was extracted with ether, washed with dilute sodium hydroxide, dried over potassium carbonate and distilled to give 6.5 g. (46% yield) of *p*-ethylbiphenyl, b. p. 149.5-149.8 (12 mm.), m. p. 33.5-34.5. Repeated recrystallization from methanol gave a material melting constantly at 34.0-34.5°, unchanged when mixed with first sample.

A third synthesis of *p*-ethylbiphenyl was effected by the aluminum chloride catalyzed ethylation of biphenyl using diethylbenzene as the alkylating agent. Using 12 mole per cent. (based on biphenyl) of anhydrous aluminum chloride as a catalyst, mixtures of diethylbenzene were vigorously stirred for several hours at temperatures ranging from 80-110°. The products were then washed with dilute solu-

(9) Lazier and Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, 1943, p. 144.

(10) Adam, *Bull. soc. chim.*, [2] **47**, 689 (1887); **49**, 101 (1888).

tions of hydrochloric acid and sodium hydroxide and distilled at high reflux ratio through a 1-meter Vigreux column giving monoethylbiphenyls,<sup>11</sup> b. p. 150–153° (13 mm.),  $n_D^{20}$  1.5925–1.5933, diethylbiphenyls, b. p. 118–122° (1.5 mm.),  $n_D^{20}$  1.5811, as well as lower boiling recovered biphenyl and mono and polyethylbenzenes.

*Anal.* Calcd. for  $C_{14}H_{14}$ : C, 92.23; H, 7.74. Found: C, 92.35; H, 7.70. Calcd. for  $C_{16}H_{18}$ : C, 91.37; H, 8.63. Found: C, 91.45; H, 8.56.

A number of alkylation experiments are summarized herewith.

Mole fraction diethylbenzene charged	Conditions	Conversion			
		Bi-phenyl, %	Monoethyl bi-phenyl, %	Diethyl bi-phenyl, %	Residue (as calcd. triethylbiphenyl), %
0.33	80° (6 hr.)	58	22	15	3
.50	90° (2 hr.)	40	33	27	4
.60	110° (1 hr.)	25	36	39	8
.70	90° (2 hr.)	28	36	31	10
.80	90° (2 hr.)	19	37	32	15

Static crystallization at 0° of the liquid mixture of monoethylbiphenyls gave about 30% solid material which was filtered and allowed to warm to room temperature on the filter, leaving about 10% of material m. p. 32–33°. This was recrystallized twice from dilute ethanol to give *p*-ethylbiphenyl, m. p. 33.8–34.5° which did not change on further recrystallization.

**3-Bromobiphenyl.**—A slight modification of the method of Scarborough and Waters<sup>12</sup> was employed for the preparation of 2-acetamino-5-bromobiphenyl. *o*-Aminobiphenyl (340 g., 2.0 moles) in 750 cc. of pyridine was treated with 214 cc. (236 g., 3.0 moles) of acetyl chloride with stirring and cooling at 10–15°. One hour after addition, the product was poured into a liter of concd. hydrochloric acid and ice, filtered, washed and dried to give a 95% yield of *o*-acetaminobiphenyl, m. p. 118–119° after recrystallization from dilute acetic acid. Seventy grams (0.33 mole) of this product in 600 cc. glacial acetic acid was treated rapidly with 17 cc. of bromine (53.1 g., 0.33 mole) in 450 cc. of acetic acid. After standing overnight, the material was poured into water, filtered and dried. A 93% yield (90 g.) of 2-acetamino-5-bromobiphenyl, m. p. 127–127.5° after recrystallization from ethanol, was obtained.

This material (585 g., 2.0 moles) was dissolved in 820 cc. of hot 95% ethanol containing 600 cc. of concd. hydrochloric acid and refluxed for four hours. The product was then poured into 6 liters of water and treated with sufficient 15% sodium hydroxide solution to liberate the free base. On cooling, the product solidified was filtered and redigested with hot water before final filtration and drying. A nearly theoretical yield (495 g.) of 2-amino-5-bromobiphenyl, melting at 53–56° was obtained.

The diazotization was adapted from the procedure of Bigelow, Johnson and Sandborn<sup>13</sup> for the conversion of 3-bromo-4-amino-toluene to *m*-bromotoluene. 2-Amino-5-bromobiphenyl (213 g., 0.8 mole) was dissolved in 650 cc. of ethanol and 116 g. of concentrated sulfuric acid added, keeping the temperature below 50°. After cooling to 5°, a cold solution of 88 g. of sodium nitrite in 100 cc. of water was added followed by 20 g. of ether-washed copper bronze. On warming gently a vigorous evolution of gases took place at 40–45° and a cooling bath was applied. When this reaction had subsided, the material was heated under reflux for two hours and steam distilled at a flask temperature of 150–180°. The 6–7 liters of steam distillate was ex-

tracted with benzene and washed successively with a dilute solution of sodium hydroxide, water and concentrated sulfuric acid. After drying over potassium carbonate the benzene solution was distilled to give *m*-bromobiphenyl, b. p. 158–167° (11 mm.),  $n_D^{20}$  1.6390 in 58% yield. Marvel, Ginsberg and Mueller<sup>6</sup> give b. p. 169–173° (17 mm.)  $n_D^{20}$  1.6411, for a product obtained in 16% yield by the coupling of *m*-bromobenzenediazonium hydroxide and benzene.

***m*-Biphenylmethylcarbinol.**—*m*-Bromobiphenyl was converted to the Grignard reagent in dry ether in the usual fashion and treated with an ether solution of acetaldehyde at 0°. After warming to room temperature, the material was hydrolyzed by an ice cold ammonium chloride solution. The product was washed, dried and distilled to give a small amount of biphenyl, b. p. 85–90° (1 mm.), and *m*-biphenylmethylcarbinol, b. p. 146–149° (1 mm.),  $n_D^{20}$  1.6098 in 66% yield.

***m*-Vinylbiphenyl.**—A benzene solution of the carbinol was dehydrated in the usual fashion at 300° and 50 mm. pressure. A 55% yield of product, b. p. 112° (1 mm.),  $n_D^{20}$  1.6263,  $d_4^{25}$  1.028, *M*<sub>R</sub>D calcd. (exclusive of exaltation), 59.58; observed, 62.09. The material froze to a glass when cooled to 80°.

***m*-Acetylbiphenyl.**—Fifteen grams of *m*-biphenylmethylcarbinol was added to a solution of 80 cc. of 10% sulfuric acid, 75 cc. of acetic acid and 15 g. of potassium bichromate at 40–45°. One hour after addition was complete, the material was quenched with a liter of water, the oil extracted with ether, washed with dilute solutions of sulfuric acid and sodium hydroxide, dried over potassium carbonate and distilled to give 12 g. (81% yield) of *m*-acetylbiphenyl, b. p. 137–138° (1 mm.),  $n_D^{20}$  1.6140. The product could not be induced to crystallize.

***m*-Ethylbiphenyl.**—*m*-Biphenylmethylcarbinol was hydrogenated in a manner similar to that used for the para isomer to give a pure product, b. p. 143° (11 mm.),  $n_D^{20}$  1.5859. An unsuccessful attempt was made to prepare this compound by the Wurtz-Fittig technique from sodium, *m*-bromobiphenyl and ethyl bromide in refluxing ether solution.

***o*-Vinylbiphenyl.**—*o*-Iodobiphenyl was prepared from *o*-aminobiphenyl by the Sandmeyer method according to the procedure of Gilman, Kirby and Kenney.<sup>14</sup> A 78% yield of material, b. p. 145–147° (6 mm.), was obtained. On one of the three runs, after about one-fourth of the potassium iodide had been added to the diazonium salt at 2–3°, an almost explosive reaction occurred in which most of the product was thrown out of the flask. The cause of this behavior was not determined since subsequent identical runs reacted normally.

The *o*-iodobiphenyl was converted to the Grignard reagent in ether solution and reacted with acetaldehyde in a manner similar to that employed for the *m*-isomer. A 79% yield of *o*-biphenylmethylcarbinol, m. p. 111–112°, was obtained by recrystallizing the crude product from a mixture of benzene and hexane. Bradsher and Wert<sup>3</sup> report m. p. 110.5–111.5° for a product similarly prepared on a smaller scale in 56% yield.

***o*-Vinylbiphenyl.**—Dehydration of an 85% dioxane solution of *o*-biphenylmethylcarbinol was effected in the usual manner at 300° and 30 mm. pressure, giving a 70% yield of product, b. p. 114–117° (1 mm.),  $n_D^{20}$  1.6168,  $d_4^{25}$  1.0261. This product was first made by Bradsher and Wert<sup>3</sup> in 24% yield by a potassium bisulfate liquid phase dehydration, to give a product, b. p. 127–130° (5 mm.).

***o*-Acetylbiphenyl.**—*o*-Biphenylmethylcarbinol was oxidized in a manner similar to that described for the meta isomer. An 88% yield of *o*-acetylbiphenyl, b. p. 157.5–158.0° (11 mm.), m. p. 56.0–56.5° was obtained.

***o*-Ethylbiphenyl.**—*o*-Biphenylmethylcarbinol was catalytically hydrogenated in a manner similar to that given for the para isomer to give a 97% yield of the *o*-ethylbiphenyl, b. p. 128–129° (11 mm.),  $n_D^{20}$  1.5758,  $n_D^{25}$  1.5710, f. p. –6°.

(11) Epelberg and Lowry, *THIS JOURNAL*, **63**, 101 (1941), report that oxidation experiments indicate that a similar preparation obtained from biphenyl, aluminum chloride and diethyl sulfate contained predominantly meta and some para isomers. Some ortho isomer does form but boils much lower, see Table I.

(12) Scarborough and Waters, *J. Chem. Soc.*, 87 (1927).

(13) Bigelow, Johnson and Sandborn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 133.

(14) Gilman, Kirby and Kenney, *THIS JOURNAL*, **51**, 2252 (1929).

### Summary

The ortho, meta and para isomers of ethylbiphenyl, acetylbiphenyl, biphenylmethylcarbinol and vinylbiphenyl have been synthesized and

characterized. *p*-Ethylbiphenyl has been shown to melt at 34° instead of 47° as previously reported. An improved synthesis of *m*-bromobiphenyl is described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

## Further Studies on Steric Deformation<sup>1</sup>

BY RUDOLPH C. ELLINGSON<sup>2</sup> AND ALSOPH H. CORWIN

In the preceding paper of this series McEwen<sup>1</sup> has recorded the preparation of N-methyl etioporphyrin I and some of its derivatives. This substance, as was pointed out, is unusual in the degree of crowding of its atoms. Because of their theoretical importance, we have examined McEwen's synthetic method and structural conclusions in greater detail. Our conclusion, reached by methods described below, is that the structure assigned to N-methyletioporphyrin I is correct and that explanations of the peculiar chemistry of this and related substances must proceed from this premise.

The work reported in this paper was performed upon N-methyletioporphyrin II because of the readier availability of this than of N-methyletioporphyrin I. In addition to confirming the position of the added methyl group on a nitrogen in the porphyrin, we have discovered two reactions which cleave the methyl group from the ring. These strengthen the hypothesis that the methylated porphyrin is highly strained and demonstrate that this strain manifests itself in decreased chemical stability of the molecule. This is a clear-cut geometrical or stereochemical effect on reactivity. Much of the energy necessary to break the ordinarily stable C-N bond is supplied in this instance by relieving the steric deformation due to the crowded position of the methyl group in the center of the molecule.

With respect to preparation, our studies confirmed McEwen's report that dimethyl sulfate does not methylate the alkali salts of the porphyrin. His method of heating the porphyrin with alkyl iodides proved the most satisfactory. Use of the di-sodium salt of the porphyrin was found, however, to hinder rather than to help the reaction. Products of high purity were obtained by chromatographic adsorption.

To secure greater analytical differentiation, an attempt was made to prepare higher N-alkyl porphyrins. Mono-N-ethyletioporphyrin II was prepared successfully but in much lower yield. The *n*-propyl and *n*-butyl derivatives could not be prepared by the iodide method.

(1) Studies in the Pyrrole Series, XVI; Paper XV, McEwen, *THIS JOURNAL*, **68**, 711 (1946).

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The constitutional problem was attacked from several angles. Carbon and hydrogen analyses for both the N-methyl and N-ethyl derivatives proved to be consistent with the postulated structures. The active hydrogen determination with methylmagnesium iodide showed the presence of only one active hydrogen instead of two as in the parent porphyrin. Compelling evidence for the acceptance of the postulated formula was finally obtained, however, by oxidative degradation of the N-methylporphyrin. The oily N-methyl-ethyl-methylmaleic imide obtained was hydrolyzed and the methylamine formed was identified. This establishes the presence of a CH<sub>3</sub>-N linkage in the porphyrin and, combined with the other evidence adduced, establishes the constitution of these alkylated porphyrins as N-alkyl porphyrins. New N-alkyl etio-porphyrins can be identified readily by the characteristic shift in the absorption spectrum. This resembles qualitatively the shift produced by the introduction of methyl groups into dipyrromethenes. The addition of two methyls to a symmetrical methene shifted the absorption maximum toward longer wave lengths by 400 Å., whereas the addition of a single methyl group in the porphyrin shifted each of the absorption bands to longer wave lengths by smaller amounts. The shifts in the four strong bands of the porphyrin, reading from the violet to the red, were +80, +50, +190, and +200 Å.

It is possible to imagine two models of an N-methyl porphyrin, one in which the methyl group is coplanar with the porphyrin ring, the other in which the CH<sub>3</sub>-N bond is bent so that the methyl group is out of the plane of the ring. Sufficient data to permit a decision between these possibilities are not now at hand. Robertson<sup>3</sup> has shown that the phthalocyanine nucleus is capable of undergoing considerable deformation to accommodate smaller and larger metals in the center of the ring. Figure 1 is a model of an N-methylporphyrin using bond angles found in Robertson's studies. The large ring has been compressed from the sides and the pyrrole rings have been compressed from the center to increase the distance between two opposite nitrogens and permit maximum accommodation of the methyl group within the lim-

(3) Robertson, *J. Chem. Soc.*, 1204 (1936); Robertson and Woodward, *ibid.*, 221 (1937); 40 (1940).