Of interest also is the very recent report[12] that the *dianion* of phloroglucinol has a ketone structure while the monoanion appears to exist exclusively as the phenolate anion.

Acknowledgment.—We wish to thank Professor T. Cohen for helpful discussions.

[12] R. J. Highet and T. J. Batterham, *J. Org. Chem.*, **29**, 475 (1964).

Methylation of Pyrrylmagnesium Bromide[1]

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In a recent study, Skell and Bean have shown that the alkylation of pyrrylmagnesium bromide (1) with a series of alkyl halides yields the isomeric 2- and 3-alkylpyrroles and polyalkylpyrroles as major products.[2] These findings confirmed the original report of Oddo[3] and refuted certain subsequent claims[4] regarding the nature of the products arising from the alkylation of **1**.[5] Skell and Bean employed only methyl bromide and tosylate as methylating agents for **1**; analysis of products was achieved by infrared analysis of distillation fractions.[2] The yields of 2-methyl- (**2**) and 3-methylpyrrole (**3**) and the conversion of pyrrole were low in these studies. Since the direct methylation of **1** represents an experimentally simple one-step synthetic entry to **2** and **3**, a reinvestigation of the methylation of **1** with methyl iodide, dimethyl sulfate, trimethyl phosphate, and methyl tosylate has been carried out under conditions different from those employed by Skell and Bean in an attempt to obtain synthetically useful yields of **2** and **3**. Product identification and analyses have been carried out by gas–liquid chromatography. The results obtained in this study are similar to those of Skell and Bean[2] with regard to both yields of **2** and **3** and utilization of **1**.

The alkylation of **1** with equimolar quantities of each of the four alkylating agents was carried out in refluxing ether (normal reaction period of 22 hr.); the reaction mixture was quenched under neutral conditions (deoxygenated water at 15°). Quenching by the use of ice and sulfuric acid[3] or aqueous ammonium chloride[6] gave poor product recovery and extensive formation of tars, presumably by the acid-catalyzed polymerization of pyrroles. The results of these methylation experiments are summarized in Table I.

Product identification and reaction mixture analyses were carried out by gas–liquid chromatography on a Carbowax 20M column, programming the column temperature from 50 to 150°. Under these conditions, pyrrole, N-methylpyrrole, **2** and **3** could be separated cleanly; each of these materials was identified by comparison of its g.l.c. behavior with that of an authentic sample and by collection of samples on elution and comparison with authentic materials. Further alkylated products (A and B, Table I) were not identified, but were separated cleanly by the g.l.c. method. Products A and B were shown not to be either 2,4- or 2,5-dimethylpyrroles by comparison of g.l.c. behavior. The authentic dimethylpyrroles had retention times slightly shorter than that of A; because of the similarity of retention times, A and B are assumed to be dimethylpyrroles or pyrrolenines. A third unidentified minor product (C) was also formed in these alkylations and was resolved cleanly and probably represents a higher methylated structure since an increase in column temperature was required for its elution. Other materials were eluted following C, but only as unresolved smears.

Methylation of 2-methylpyrrylmagnesium bromide with methyl iodide under the standard conditions of Table I led to extensive methylation (30% recovery of **2**); both compounds A and B were present as minor reaction products. Attempted methylation of 2,5-dimethylpyrrylmagnesium bromide under the standard conditions was unsuccessful; an almost quantitative recovery of the starting pyrrole was obtained. Under different reaction conditions, Johnson has observed the methylation of this Grignard reagent; 2,3,4,5-tetramethylpyrrole and tetramethylpyrrolenines were the major products.[6]

An examination of the results presented in Table I shows that the general conclusions of Skell and Bean[2] have been substantiated by this study. The major products of the reaction are **2** and **3**, obtained in ratios (**2** to **3**) of 1.3 to 3.1. With the exception of trimethyl phosphate which shows little selectivity, alkylation of the 2-position of **1** is favored by a factor of at least two. In contrast to the results of Skell and Bean[2] and earlier workers,[3,4] minor amounts of N-methylpyrrole were obtained; however, the analytical technique employed by these workers probably would not have allowed the detection of such minor amounts of material. Although the formation of the N-methylated product has not been observed previously, some degree of alkylation at this position might be expected since **1** has been shown to exist as either an N–MgX structure or a resonance-stabilized anion with the negative charge distributed between carbon and nitrogen.[7] In contrast, the N-alkylation of the alkali metal derivatives of pyrrole is well known.[8] Additionally, significant amounts of the higher methylated species A and B are also formed. The formation of A and B in the methylation of 2-methylpyrrylmagnesium bromide indicates these materials to possess a minimum of one 2-methyl group.

The observed increase in methylating ability [$CH_3I < (CH_3)_3PO_4 < (CH_3)_2SO_4 \cong CH_3OTs$] of the reagents studied follows the general trend observed for their reactivity toward Grignard reagents and carbanions.[9] Relatively little use has been made previously of the alkylating ability of trimethyl phosphate in Grignard

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[1] This study was supported in part by a grant from the Health Research and Services Foundation.

[2] P. S. Skell and G. P. Bean, *J. Am. Chem. Soc.*, **84**, 4655 (1962).

[3] B. Oddo and R. Mameli, *Gazz. chim. ital.*, **43II**, 504 (1913).

[4] K. Hess and F. Wissing, *Ber.*, **47**, 1416 (1914).

[5] For a summary of references regarding the alkylation of **1**, see ref. 2.

[6] H. Booth, A. W. Johnson, E. Markham, and R. Price, *J. Chem. Soc.*, 1587 (1959).

[7] M. G. Reinecke, H. W. Johnson, and J. F. Sebastian, *J. Am. Chem. Soc.*, **85**, 2859 (1963).

[8] P. A. Cantor and C. A. Vanderwerf, *ibid.*, **80**, 970 (1958).

[9] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, Chapters XVI and XX; C. M. Suter and H. L. Gerhard, *J. Am. Chem. Soc.*, **57**, 107 (1935); J. M. Conia, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 43 (1963).

TABLE I

METHYLATION OF PYRRYLMAGNESIUM BROMIDE

	Alkylating agent									
Product	CH_3I	CH_3Br	$(CH_3)_2SO_4$	$(CH_3)_3PO_4$	CH_3OTs					
	Reaction time, hr.									
	22	48[a]	22	22	3	6	12	22	48	0.25
	Yield or Recovery, %									
Pyrrole	39.4	40.7	40.0	52.1	42.5	42.1	46.5	33.8	40.0	41.2
2-Methylpyrrole	8.9	10.4	21.8	13.5	27.5	25.3	24.5	22.4	20.2	19.6
3-Methylpyrrole	3.9	5.5	10.0	10.4	13.2	10.8	7.9	9.4	8.6	9.2
A	2.1	...	3.4	1.6	5.2	5.8	3.8	6.0	4.6	...
B	8.8	...	6.7	6.8	6.7	11.0	9.5	6.4	2.2	...
N-Methylpyrrole	0.0	0.0	1.0	0.6	1.0	0.7	0.8	...	0.7	0.0
	Total Recovery, %									
	63.0	69	82.6	85.0	96.0	95.6	93.0	78.2	75.1	89
	Product Ratio, 2-Methyl- to 3-Methyl-									
	2.3	1.9	2.2	1.3	2.1	2.3	3.1	2.4	2.5	2.1

[a] See ref. 2.

chemistry. Gilman has shown the compound to be effective in the methylation of hindered Grignard reagents such as mesitylmagnesium bromide,[10] and Polsky has reported a related alkylation of 2,5-dimethylpyrrylmagnesium bromide.[11] The results of this study indicate the reagent to be considerably more effective than either methyl iodide or bromide in reaction with **1**.

The effect of reaction time, in the case of methyl tosylate, on the yields of distribution of products follows reasonable expectation in view of the results of Johnson.[6] The total recovery and yields of **2**, **3**, A, and B decrease with reaction time indicating a gradual accumulation of polymethylated products. These reresults are consistent with and support the concept of an equilibrium between **1** and the methylated pyrroles (**2**, **3**, A, and B). Grignard exchange would lead to methylated pyrrylmagnesium bromides, which because of the cumulative inductive effects of the methyl groups, would undergo methylation more rapidly than **1**. Such an interpretation has been advanced previously by Johnson to account for the results observed in the alkylation of 2,5-dimethylpyrryl Grignard reagents[6] and is consistent with the results observed in this study. The statistical inferences of such an equilibrium would require an initial slow methylation of **1** to form **2** and **3** followed by a more rapid methylation of **2** and **3** to yield A, B, and higher methylated products.

The results of the 3-hr. experiment with methyl tosylate indicates the possibility of synthetic utilization of the methylation of **1**. In this experiment, the yields of **2** (27.5%) and **3** (13.2%) are the maximum observed, and the high total recovery of material indicates polymethylation to be negligible. The relative simplicity of product distribution in this experiment indicates that the use of even shorter reaction periods and more powerful methylating agents, *e.g.*, $(CH_3)_3O^+BF_4^-$, may result in a useful synthetic method for the preparation of monomethylpyrroles.

Experimental[12]

Methylation of Pyrrylmagnesium Bromide (1).—A solution of pyrrole (0.215 mole) in 50 ml. of ether was added over a period of 40 min. to a solution of ethylmagnesium bromide (0.215 mole) in 75 ml. of ether. The reaction mixture was refluxed for 2 hr. with an additional 80 ml. of ether being added during the period of reflux. After cooling the reaction mixture to 5°, the alkylating agent (0.215 mole) in 50–75 ml. of ether was added. After the dropwise addition of the alkylating agent was completed, the reaction mixture was refluxed for the times indicated in Table I. The reaction mixture was cooled in an ice–salt bath to below 10° and quenched by the dropwise addition of 250 ml. of ice-cold deoxygenated water; the temperature of the reaction mixture was maintained below 15°. Distilled water was deoxygenated by the passage of nitrogen for 5 to 10 min. After the addition of water was completed, the aqueous layer was extracted with cold ether until the ether extracts were clear. The combined ethereal layers were then washed with cold deoxygenated water until the aqueous washes were either neutral or slightly basic (pH 7.0–7.5). The aqueous extracts were treated with dilute sulfuric acid to a pH of 7.0–7.5 and extracted with ether; the combined ethereal extracts were dried over anhydrous magnesium sulfate at 15° and concentrated under reduced pressure at temperatures below 25°.

Gas–Liquid Chromatographic Analysis and Product Identification.—The reaction mixture concentrates (2-μl. samples) were analyzed on a 30% Carbowax 20M column with Chromosorb P (60–80 mesh) as support with a helium flow rate of 46–47 ml./min. and an injection port temperature of 185°. The column temperature was programmed manually: 0 min., 50°; 12 min., 75°; 30 min., 100°; 64 min., 125°; 72 min., 150°. Under these conditions, the products listed in Table I were resolved cleanly with the following observed retention times (min.): N-methylpyrrole, 18.5; pyrrole, 55.0; **2**, 59.0; **3**, 62.5; A, 67.5; B, 69.5. Quantitative analysis was carried out by Disc integration of peak areas with the raw results being corrected by the response sensitivity of the appropriate component. The sensitivity of each component being analyzed was determined by triplicate determinations of the peak areas produced by known amounts of each of the components; pyrrole was employed as a reference (sensitivity = 1.0). Typical relative sensitivities are N-methylpyrrole, 1.16; 2-methylpyrrole, 0.80; 2,5-dimethylpyrrole, 0.74; 2,4-dimethylpyrrole, 0.71. The products (pyrrole, N-methylpyrrole, **2**, and **3**) were identified by comparison of the g.l.c. behavior of authentic samples, "spiking" of reaction mixtures, and comparison of the infrared spectra of trapped eluted fractions with those of authentic samples of the appropriate materials. The absence of 2,4- and 2,5-dimethylpyrroles in the reaction mixtures was demonstrated by "spiking" reaction mixtures with authentic samples of the pyrroles. Pyrrole and N-methylpyrrole were commercial products. 2-Methylpyrrole was prepared from 2-formylpyrrole (Beacon Chemical Industries, Inc.)

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(10) H. Gilman and B. J. Gai, *J. Am. Chem. Soc.*, **82**, 6326 (1960).

(11) R. A. Polsky, M.S. Thesis, University of Pittsburgh, 1961.

(12) Infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer using either dilute solutions in 0.1-mm. cells or thin films between sodium chloride plates. Gas–liquid chromatographic analyses were carried out with an F and M Model 500 gas chromatograph equipped with a Disc integrator.

by a Wolff–Kischner reduction.[13] 2,5- and 2,4-dimethylpyrroles were prepared by established procedures.[14] All pyrroles were distilled to obtain center fractions and stored under nitrogen at 5° until used.

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[13] A. I. Vogel, "Practical Organic Chemistry," 3rd. Ed., Longmans, Green and Co., London, 1956, p. 510.

[14] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 219.

Two Cases of Unexpected Formation of the Fluoranthene System

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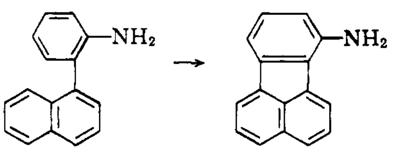
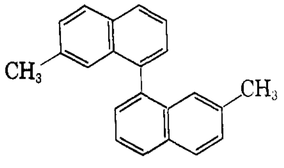
When 1-(2-aminophenyl)naphthalene (I) was treated successively with boron trichloride in boiling benzene and with aluminum chloride at 120°, a boron-free compound, $C_{16}H_{11}N$, was formed. It was a primary amine and was converted by deamination into fluoranthene. Also the spectrum of the nitrogenous compound was practically identical with that of fluoranthene. In accordance with the following equation it can be assumed that the amine is 9-aminofluoranthene (II). The dehydrogenation which takes place is facilitated by the fact that it removes the mutual interference of the hydrogen atoms in the 6-position of the aminophenyl group and the 8-position of the naphthalene system.



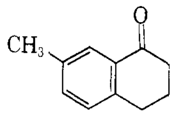
I II

For the synthesis of some complex polycyclic compounds, 7,7′-dimethyl-1,1′-dinaphthyl (III) was required. To this end, 7-methyl-1-tetralone[1] (IV) was reduced with aluminum amalgam to the corresponding pinacol V and the latter, after careful washing, was dehydrated and dehydrogenated. The hydrocarbon (III), $C_{22}H_{18}$, formed colorless needles and absorbed, as expected, at 287 and 296 mμ. When, however, the *crude* (unwashed) pinacol V was dehydrated, a yellow hydrocarbon, $C_{22}H_{16}$, was obtained. Its ultraviolet spectrum was identical, apart from a slight bathochromic shift, with that of benzo[*j*]fluoranthene.[2] It is thus reasonable to assume that the compound is 6,11-dimethylbenzo[*j*]fluoranthene (VI).

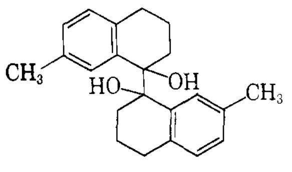
Benzo[*j*]fluoranthene had been described originally[3] as colorless, but this was corrected later[4]; the hydrocarbon was yellow.



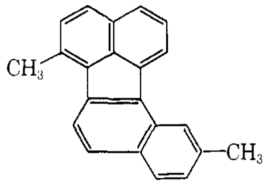
III



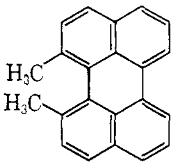
IV



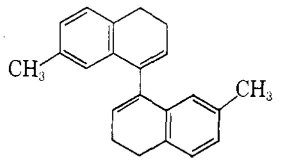
V



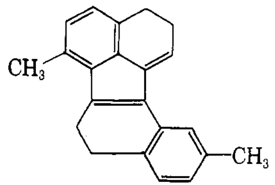
VI



VII



VIII



IX

The reaction described could have given an alternative structure, *viz.*, that of perylene derivative (VII); however, the spectrum of perylene is very different from that of our hydrocarbon. Moreover, a similar formation of a fluoranthene system from a 1-phenylnaphthalene derivative had been described before by Cook and Lawrence.[5] The cyclization which is involved in the formation of VI does not take place in the dehydrogenation step. The dehydration products, obtained from pure and crude pinacol V, respectively, are different and have, therefore, probably the structures VIII and IX.[6]

Experimental

1-Iodonaphthalene[7].—At a temperature not exceeding 5°, a solution of 25.4 g. of 1-naphthylamine in 300 ml. of water and 100 ml. of concentrated hydrochloric acid was diazotized with 7.0 g. of sodium nitrite. A solution of 17 g. of potassium iodide in 50 ml. of water was added and, after 1 hr. at room temperature, the mixture was heated on the water bath for 10 min. and made alkaline. The mass was extracted with benzene and the solvent was evaporated. Distillation of the residue with steam gave a product which was washed with sodium bisulfite solution and water, dried, and distilled: b.p. 168° (2 mm.), yield 18%.

1-(2-Nitrophenyl)naphthalene.—At a temperature of 200°, 12 g. of copper powder was added to a well-stirred mixture of 7 g. of 1-iodonaphthalene and 6 g. of 2-bromonitrobenzene. The temperature was then raised to 250° for a period of 5 hr., and the cooled mixture was extracted repeatedly with 80 ml. of hot benzene. The desired product boiled at 168–173° (2 mm.) and crystallized upon treatment with methanol. Recrystallization from the same solvent gave 2.2 g. (30%) of yellow platelets, m.p. 95° (lit.[8] m.p. 88–90°).

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[2] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc, New York, N. Y., 1951, No. 542.

[3] M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **69**, 505 (1947).

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[6] A short communication has been published before [E. D. Bergmann and P. Bracha, *Bull. Res. Council Israel*, **11A**, 27 (1962)].

[7] *Cf.* F. Noelting, *Ber.*, **19**, 135 (1886).

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