TABLE III

REACTION OF ALCOHOLS OVER NICKEL CATALYST Ni-0104T

	Products, mole %						
Alcohol	Carbon dioxide	Carbon monoxide	Methane	Ethane	Propane	Propene	Butane
Methanol	23.70	...	69.40	...	...	...	...
Ethanol	24.00	0.60	69.00	2.00	4.00	...	...
1-Propanol	18.70	...	41.10	36.10	...	...	...
1-Butanol	11.54	0.71	18.72	3.05	61.23	0.66	2.65

during this reaction. There was no conversion of the alcohols when passed through the reactor under the same conditions but in the absence of a catalyst. The results of this study are summarized in Table III.

We suggest that the mechanism of this vapor phase alkylation follows the same mechanism postulated by Reinecke and Kray.[8] The formation of the next lower hydrocarbon when alcohols were passed over our catalyst suggests dehydroxymethylation *via* dehydrogenation to aldehyde and loss of carbon monoxide. Formation of carbon monoxide is further supported by the work of Bonner and Greenlee[9] who found it adsorbed on Raney nickel after refluxing with ethanol. The fact that carbon monoxide is not found in gases from passing an alcohol over the catalyst is probably because it never leaves the catalyst surface as such. It reacts with hydrogen and the pyridine adsorbed on the catalyst surface to yield the α-substituted pyridine or with hydrogen alone to yield methane. The water produced in these reactions also reacts with carbon monoxide with formation of carbon dioxide and hydrogen. Similar cleavage of molecules with intermediary formation of carbon monoxide probably occurs with the other reagents employed in this study. As suggested by Reinecke and Kray,[8] the specificity of alkylation on the α position may be related to the orientation of the pyridine nucleus to the catalyst surface through the free electron pair on the nitrogen. Work is underway to elaborate further the mechanisms of these reactions.

Experimental Section

Mass spectra were obtained with a Model 21-103-C spectrometer (Consolidated Electrodynamics Corp.). Gas chromatographic analyses were carried out with an F and M Model 609 chromatograph using a column of 20% silicone grease (Dow-Corning) suspended on Chromosorb W.

Reactions were carried out in the vapor phase using steel or glass tubes, 1.25-in. i.d., having a heated length of 36 in. The catalyst volume in all reactions was 550 ml. The glass tube was heated with electrically heated blocks. The steel tube was immersed in an electrically heated Dowtherm bath. The pyridine compound and the alkylating agent were mixed in the desired molar ratios and fed to the reactor through a vaporizer preheater with a metering pump. When methane or the carbon monoxide-hydrogen mixture were used as alkylating agents, they were fed through calibrated flow meters. Rates of feed were calculated to give the indicated contact times assuming that the reactants obeyed perfect gas laws. Vapors leaving the reactor were passed through a water-cooled condenser and liquid products collected. The product was freed of water by contacting with solid potassium hydroxide and distilled in a spinning-band column. The fractions from the distillation were analyzed by gas chromatography and components were identified by their retention times and their infrared spectra

The catalysts found useful in this reaction contained 60-70% nickel. Two commercially available catalysts, Ni-0104T and Ni-1404T (Harshaw Chemical Co., Cleveland, Ohio), were found to be especially suitable.

Acknowledgement.—We wish to thank Dr. J. Block, Union Carbide European Research Associates, and Professor H. House, Massachusetts Institute of Technology, for helpful suggestions, and Messrs. R. V. Price and D. R. Morrison for technical assistance.

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[9] W. A. Bonner and T. W. Greenlee, *J. Am. Chem. Soc.*, **81**, 2122 (1959).

Preparation and Properties of 1,4-Dihydronaphthalen-1,4-imines

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It has been shown that benzyne reacts with N-substituted 2,5-dimethylpyrroles to form substituted 2-naphthylamines,[1] whereas benzyne with N-benzyl-2,3,4,5-tetramethylpyrrole gives the stable 1,2,3,4-tetramethyl-1,4-dihydro-1,4-(N-benzylimino)naphthalene.[2] We now report on the preparation and properties of several other stable imines, all made from fully substituted pyrroles, in which the N substituent is phenyl, cyclohexyl, or *n*-butyl.

The pyrroles were prepared by the method reported earlier[1] and were found to be very susceptible to air oxidation. The pyrrole-benzyne adducts were prepared essentially as already described,[2] but using improved methods for isolating the imines.

Titration of the basic imines with perchloric-acetic acid gave fairly accurate estimates of their equivalent weights, and potentiometric titration in aqueous methanol solutions gave their pK_a values. Very dilute aqueous acid solutions of the imines at room temperature are stable for a short time, but on standing for an hour or more the imines gradually react to form the same compound, 1-(hydroxymethyl)-2,3,4-trimethylnaphthalene, and the amine from which the pyrrole was made. On the other hand, hot aqueous acids convert these imines to bis[2,3,4-trimethylnaphthyl-(1)-methyl] ether[3] and the amine. Furthermore, in methanol as solvent, acids convert the imines to 1-(methoxymethyl)-2,3,4-trimethylnaphthalene.[3] All of these reactions clearly indicate the similarity of these imines and the epoxides.[3]

These reactions also support the idea suggested earlier[3] that the oxygen atom of the epoxides, and now the nitrogen atom of the imines, is completely detached from the parent compound when treated with acids,

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[1] E. Wolthuis, D. VanderJagt, S. Mels, and A. DeBoer, *J. Org. Chem.*, **30**, 190 (1965).

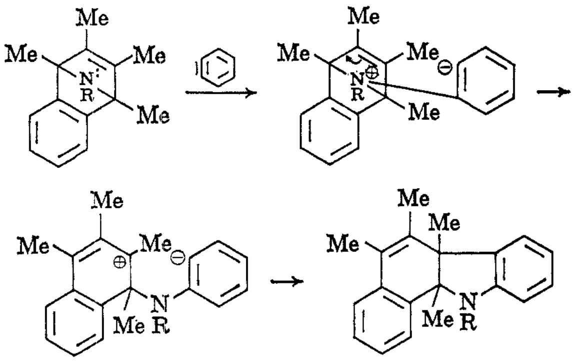
[2] E. Wolthuis and A. DeBoer, *ibid.*, **30**, 3225 (1965).

[3] E. Wolthuis, B. Bossenbroek, G. DeWall, E. Geels, and A. Leegwater *ibid.*, **28**, 148 (1963).

and the resulting carbonium ion is attacked by the solvent nucleophile. The significance of the solvent in reactions of this kind was shown recently by Fetizon, who reported that aqueous acid containing O^{18} reacts with 1,4-dimethyl-1,4-epoxy-1,4-dihydronaphthalene to give 1,4-dimethyl-2-naphthol containing the O^{18} atom.[4]

The reaction of benzyne with pentamethylpyrrole did not give the expected imine, but a product which was an adduct of 2 moles of benzyne with 1 mole of the pyrrole. Analytical and spectral data indicate the compound to be 11-methyl-6a,11a-dihydro-5,6,6a,11a-tetramethyl-11H-benzo[*a*]carbazole (**1c**). It is probably formed by nucleophilic attack of the imine first formed on another molecule of benzyne, with subsequent rearrangement to the benzocarbazole, as suggested by Wittig, who found that benzyne and N-methylpyrrole gave 11-methyl-6a,11a-dihydro-11H-benzo[*a*]carbazole.[5] To test the theory that the benzocarbazole is the result of such a secondary reaction, we have generated benzyne in the presence of previously prepared imines, N-*n*-butyl- and N-cyclohexyl-, and have obtained fairly good yields of the expected benzocarbazoles, presumably formed as shown in Scheme I.

SCHEME I



1a, R = *n*-Bu
b, R = C_6H_{11}
c, R = Me

Experimental Section[6,7]

Pentamethylpyrrole.—A mixture of 3,4-dimethyl-2,5-hexanedione (28.4 g, 0.2 mole), methylamine hydrochloride (20.1 g, 0.3 mole), anhydrous sodium acetate (24.6 g, 0.3 mole), and ligroin (bp 100–115°, 200 ml) was refluxed until all product water was removed by means of a Barrett water trap. The solution was decanted from residual salts, evaporated under reduced pressure, and the oil (22 g) was purified by steam distillation in the presence of a little sodium bisulfite to retard oxidation. The distillate containing the white, crystalline product was filtered, and the product was dried *in vacuo* at room temperature: 18 g (66%), mp 65–66°. Sublimation gave a pure sample, mp 70–70.5° (lit. mp 72°,[8] 69–70°[9]).

1-(*n*-Butyl)-2,3,4,5-tetramethylpyrrole.—A mixture of 3,4-dimethyl-2,5-hexanedione (28.4 g, 0.2 mole), *n*-butylamine (14.6 g, 0.2 mole), and ligroin (75 ml) was refluxed until all product water had been removed by a Barrett water trap. After the solvent had been removed, the pyrrole was distilled *in vacuo* to give 22.8 g (64%), bp 86–87° (2 mm), $n^{20}{}_D$ 1.487.

Anal. Calcd for $C_{12}H_{21}N$ (178.3): N, 7.82. Found: N, 7.07.

1-Cyclohexyl-2,3,4,5-tetramethylpyrrole.—When this product was prepared as above, but with cyclohexylamine, there was obtained 17.0 g (41.3%), bp 104–116° (2 mm). Redistillation gave an analytical sample, bp 104–105° (2 mm), mp 42.0–42.8°, $n^{20}{}_D$ 1.517.

Anal. Calcd for $C_{14}H_{23}N$ (205.3): N, 6.83. Found: 6.94.

1-Phenyl-2,3,4,5-tetramethylpyrrole.—Using aniline as amine, the above procedure gave 31.1 g (76.3%), bp 142–144° (12 mm) [lit. bp 140° (18 mm),[10] 60° (0.3 mm)[8]], $n^{20}{}_D$ 1.558 (lit.[8] $n^{20}{}_D$ 1.5588).

1,2,3,4-Tetramethyl-1,4-dihydro-1,4-(N-*n*-butylimino)naphthalene.—The adduct was prepared from benzyne and 1-butyl-2,3,4,5-tetramethylpyrrole (17.9 g, 0.1 mole) essentially by the previously described method,[2] but was isolated as follows. The solution was decanted from unreacted magnesium, washed with saturated aqueous ammonium chloride containing a little ammonium hydroxide, dried over potassium carbonate, and distilled to remove the solvent. The residual oil (19.4 g) was dissolved in hexane; the solution was clarified and then extracted with a total of 2 l. of 0.1 *M* hydrochloric acid. Without delay, the acid extracts were combined and neutralized with sodium hydroxide to release the imine, which was extracted with hexane. After drying the solution over potassium carbonate, the solvent was removed, and the product was fractionated to give 16.0 g (63%), bp 133–135° (2 mm). An analytical sample distilled at 134.5° (2 mm): $n^{20}{}_D$ 1.528; $\lambda_{max}^{cyclohexane}$, mμ (log ε), 270 sh (3.35), 276 (3.42), 283 (3.36). Its infrared spectrum showed several bands at 1000–1200 cm^{-1} (C–N stretch); its nmr spectrum (deuteriochloroform) showed signals at δ 1.54 and 1.60 (two pairs of methyl groups), a triplet at δ 2.03 ($N-CH_2$) and 7.00 (Ar–H), with the proper proton distribution.

Anal. Calcd for $C_{18}H_{25}N$ (255.4): N, 5.49. Found: N, 5.68.

Acidimetric titration[11] gave the equivalent weight 256. Potentiometric titration in methanol–water (4:1) under nitrogen at 25° gave $pK_a = 8.46 \pm 0.08$ (average of six values).

The hexane solution left from the acid extraction was clarified with carbon and evaporated to leave 0.70 g of an oil, which was dissolved in benzene and chromatographed on alumina to give 0.05 g, mp 84–84.5°, which proved to be identical with **1a** as shown by mixture melting point and infrared spectra.

1,2,3,4-Tetramethyl-1,4-dihydro-1,4-(N-cyclohexylimino)naphthalene.—On similar preparation, but with 1-cyclohexyl-2,3,4,5-tetramethylpyrrole, there was obtained 16.5 g (59%), mp 59.5–60.5°. Recrystallization from hexane gave mp 60.9–61.9°, $\lambda_{max}^{methanol}$, mμ (log ε), 276 (3.08); the infrared spectrum showed the C–N stretch bands at 1100–1200 cm^{-1}; its nmr spectrum showed absorptions at δ 1.50 and 1.58 (two pairs of methyl groups), multiplets centered at δ 1.08 and 2.58 (aliphatic protons) and 6.79 (Ar–H), with proton count of the proper order.

Anal. Calcd for $C_{20}H_{27}N$ (281.4): C, 84.41; H, 9.61; N, 4.98. Found: C, 84.75; H, 9.66; N, 5.10.

Acidimetric titration gave molecular weight 283, and potentiometric titration as above gave $pK_a = 9.32 \pm 0.07$.

1,2,3,4-Tetramethyl-1,4-dihydro-1,4-(N-phenylimino)naphthalene.—The adduct was prepared as above but, owing to its greater sensitivity to acids, was isolated as follows. The warm solution was decanted from unreacted magnesium, washed with aqueous ammonium chloride solution, and dried, and the solvent was removed. The residue was recrystallized from hexane to give 14.0 g (51%), mp 118–120°. Another crystallization from hexane gave rods: mp 121.7–122.1°; $\lambda_{max}^{methanol}$, mμ (log ε), 206 (4.55), 268 (3.14); its infrared spectrum showed C–N strectch bands at 1000–1250 cm^{-1}; nmr signals appeared at δ 1.6 and 1.65 (two pairs of methyl groups), and a multiplet centered at δ 7 (aromatic H), with proper proton distribution. The pK_a, determined as above, was 5.33 ±0.1.

Anal. Calcd for $C_{20}H_{21}N$ (275.4): C, 87.2; H, 7.69; N, 5.09. Found: C, 87.18; H, 7.75; N, 5.37.

11-Butyl-6a,11a-dihydro-5,6,6a,11a-tetramethyl-11H-benzo[*a*]carbazole (1a).—Magnesium turnings (1.50 g, 0.06 g-atom) were added to a flask, which was then evacuated and filled with nitrogen. There was added dry THF (10 ml), and then about 10% of

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(4) M. Fetizon and N. Trong, *Bull. Soc. Chim. France*, 3209 (1965).

(5) G. Wittig and W. Behnisch, *Ber.*, **91**, 2358 (1958).

(6) The authors thank Dr. G. Slomp and his associates at the Upjohn Co., Kalamazoo, Mich., for their assistance in obtaining and interpreting the nmr spectra.

(7) Melting points are corrected. Nmr spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as internal standard, and the ultraviolet and infrared spectra were determined on Beckman DB and Perkin-Elmer 21 instruments, respectively.

(8) R. Griegee and M. Krieger, *Ber.*, **98**, 387 (1965).

(9) R. K. Olsen and H. Snyder, *J. Org. Chem.*, **28**, 3052 (1963).

(10) R. Ryan and N. P. Buu-Hoi, *ibid.*, **24**, 372 (1959).

(11) E. F. Hillenbrand and C. A. Pentz, in "Organic Analysis," Vol. III, J. Mitchell, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 145.

a solution of *o*-bromofluorobenzene (8.8 g, 0.05 mole) in THF (15 ml). Addition of a crystal of iodine and warming started the reaction. A solution of 1,2,3,4-tetramethyl-1,4-dihydro-1,4-(N-*n*-butylimino)naphthalene (12.8 g, 0.05 mole) in THF (15 ml) was added, and the mixture was heated to 65–70°. At this temperature the remaining *o*-bromofluorobenzene solution was added during 1.5 hr, and the solution was refluxed 3 hr more. Upon cooling, it was extracted with 150 ml of saturated aqueous ammonium chloride, the THF layer was dried over potassium carbonate, and the solvent was removed under reduced pressure. The remaining solid (16 g) was dissolved in hexane, and the solution was extracted several times with a total of 2 l. of 0.1 *N* hydrochloric acid to remove any unreacted imine (3.4 g of imine was recovered on neutralizing the acid). The hexane solution was washed free of acid, dried, evaporated to about 20 ml, and refrigerated several days. After filtering off the crystalline product, further concentration of the liquors gave additional product, for a total of 4.30 g, mp 83.5–84.5°. The final liquors were chromatographed on alumina to give an additional 4.0 g, mp 68–75°. Two recrystallizations from methanol gave an analytical sample, mp 84.5–85.3°.

Anal. Calcd for $C_{24}H_{29}N$ (331.5): N, 4.23. Found: N, 4.44.

Its nmr spectrum showed signals of a multiplet centered at δ 0.55 (terminal methyl), 1.16 and 1.19 (tertiary methyls), 1.64 and 2.00 (Ar methyls), a triplet at δ 2.80 (N-CH_2), and several at δ 6.27–7.56 (Ar-H), with proper proton count. The ultraviolet spectrum had λ_{max}^{MeOH}, mμ (log ϵ), 220 sh (4.48), 226 sh (4.34), 257 (4.42), and 310 sh (3.45).

11-Cyclohexyl-6a,11a-dihydro-5,6,6a,11a-tetramethyl-11H-benzo[*a*]carbazole (1b).—Using the imine, 1,2,3,4-tetramethyl-1,4-dihydro-1,4-(N-cyclohexylimino)naphthalene, **1b** was prepared as in the procedure just described: 5.6 g (31.4%), mp 109–110°. Recrystallization from methanol–benzene gave rhombs: mp 110.8–111.3°; λ_{max}^{MeOH}, mμ (log ϵ), 220 (4.39), 228 sh (4.26), 262 (4.33), and 310 sh (3.34). The nmr spectrum showed signals at 1.11 and 1.40 (tertiary methyls), 1.53 and 1.96 (Ar methyls), 2.73 (N-CH), and several at δ 6.44 to 7.61 (Ar-H), with proper proton distribution.

Anal. Calcd for $C_{26}H_{31}N$ (357.5): N, 3.92. Found, 4.13.

11-Methyl-6a,11a-dihydro-5,6,6a,11a-tetramethyl-11H-benzo[*a*]carbazole (1c).—Unlike the preceding benzocarbazoles, this one was not prepared deliberatedly from benzyne and the imine, since the latter had not been isolated. Instead, it appeared as one of the products of the reaction of benzyne with pentamethylpyrrole (0.1 mole) by the procedure described above for the preparation of the imines. The hexane solution of the reaction products was not extracted with acid, but was concentrated and cooled to give 1 g of crystals, which were recrystallized from methanol to give mp 147–147.5°; λ_{max}^{MeOH}, mμ (log ϵ), 227 (4.40), 255 (4.41), and 272 sh (4.12). Its nmr spectrum showed signals at δ 1.15, 1.23, 1.67, 2.01, and 2.39 (five kinds of methyl groups), and several at 6.28–7.53 (Ar-H).

Anal. Calcd for $C_{21}H_{23}N$ (289.4): C, 87.2; H, 8.01; N, 4.84. Found: 87.43; H, 8.11; N, 4.71.

Reaction of the Imines with Aqueous Acid at Room Temperature.—The imine (1 g) was dissolved in 0.11 *N* hydrochloric acid (100 ml). Within about 1 hr the solution became turbid, and, on standing, increasing amounts of crystals appeared, which were filtered and recrystallized from methanol to give thin rods, mp 177–177.5°, identified as 1-(hydroxymethyl)-2,3,4-trimethylnaphthalene: λ_{max}^{MeOH}, mμ (log ϵ), 228 sh (4.15), 233 (5.12), 272 sh (3.61), 283 sh (3.78), 291 (3.84), and 300 sh (3.72). Its infrared spectrum showed strong hydroxyl absorption at 3300 cm^{-1}, which disappeared on acetylation. Its nmr spectrum showed signals at δ 2.42, 2.52, and 2.63 (three aryl methyl groups), 5.18 (CH_2O), and a multiplet centered at about δ 7.37 (Ar-H).

Anal. Calcd for $C_{14}H_{16}O$ (200.3): C, 83.9; H, 8.05. Found: C, 83.2; H, 8.29.

Its acetyl derivative had mp 72–73°; the compound was found to be identical with that formed by the reaction 1-(chloromethyl)-2,3,4-trimethylnaphthalene[3] with silver acetate.

Reaction of the Imines with Boiling Aqueous Acid.—A solution of the imine (0.5 g) in 2 *N* hydrochloric acid was refluxed 3 hr, cooled, and filtered; the crystals were washed with dilute acid and dried. The product, mp 172–183°, was recrystallized from methanol to give mp 189.5–190°, identified by mixture melting point and infrared spectrum to be bis[2,3,4-trimethylnaphthyl-(1)-methyl] ether.[3] The same product was obtained by boiling a mixture of the alcohol (above) and 2.8 *N* hydrochloric acid for 7 hr. The yields were 75–80% of theoretical.

Reaction of the Imines with Methanolic Hydrochloric Acid.—A solution of the imine (about 0.5 g) in methanol (5 ml) was treated with 5 drops of concentrated hydrochloric acid, and then refluxed 4 hr after which it was poured into 100 ml of water containing 4 g of sodium carbonate. The precipitate was extracted with hexane, the solution was extracted several times with dilute acid to remove unreacted imine (usually only a trace), and the hexane was removed to leave the product, mp 76.5–77° (methanol crystallization). Mixture melting point and infrared spectrum showed it to be 1-(methoxymethyl)-2,3,4-trimethylnaphthalene.[3]

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Friedel–Crafts Oxygenation of Aromatic Ethers, Biphenyl, and Naphthalene with Diisopropyl Peroxydicarbonate[1,2]

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Direct electrophilic oxygenation has been effected with various types of peroxides.[3] Particularly with the simpler aromatic substrates, low yields of monohydric phenols resulted because of continued oxidation. Recently, we found that use of diisopropyl peroxydicarbonate under Friedel–Crafts conditions produced controlled monooxygenation with essentially no undesirable side reactions.[4,5] The best yields of phenolic product were observed with the highly active aromatic reactants, such as, anisole and pentamethylbenzene.[5] The present study is concerned with extension of the diisopropyl peroxydicarbonate oxygenation to other types of aromatic compounds, *e.g.*, naphthalene, biphenyl, and chlorobenzenes. Primary attention was devoted to a more extensive investigation of the aromatic ethers.

In general, the reactions were carried out in *o*-dichlorobenzene solvent at 0–5° with a catalyst to peroxide ratio of 2. The results from the aromatic ethers are summarized in Table I, and the data for the other types of aromatic substrates are set forth in Table II. The oxygenated products from the aromatic ethers and naphthalene were present in the reaction mixture in the form of the corresponding aryl isopropyl carbonate esters, as was noted previously in the case of anisole.[5] However, with biphenyl and the halobenzenes, the oxygenated material appeared to be of the type, $ArOCO_2AlCl_2$, presumably derived from cleavage of the initially formed ester. Facile ester degradation during reaction is also characteristic of the toluene system.[4] In all cases the oxygenated materials were converted to the phenolic stage by hydrolysis. Some of the identification data for the phenols is summarized in Table III.

(1) Paper III of the series, Aromatic Oxygenation.

(2) From the forthcoming Ph.D. Thesis of M. E. Kurz.

(3) See ref 4 and 5 for literature surveys.

(4) P. Kovacic and S. T. Morneweck, *J. Am. Chem. Soc.*, **87**, 1566 (1965).

(5) P. Kovacic and M. E. Kurz, *ibid.*, **87**, 4811 (1965).