amount of base used was not sufficient to neutralize the aniline sulfate.) The ether was distilled from the extract, after which the residue was sublimed at 80° and high vacuum. Recrystallization of the sublimate from ethanol gave 0.139 g (76%) of yellow prisms, mp 123–125°. The infrared spectrum of this material was identical with that of an authentic sample of 1,4-naphthoquinone.

To the aqueous solution presumed to contain the aniline sulfate was added 5 *N* sodium hydroxide solution until the phenolphthalein end point was reached. The oil layer was then removed by benzene extraction, and the extract was dried by distilling the water–benzene azeotrope. To the hot benzene solution was then added 10 ml of acetic anhydride. The solution was distilled at reduced pressure until a white crystalline residue remained. The residue was recrystallized from a benzene-isooctane solution to yield 0.266 g (85%) of acetanilide, mp 113.5–114.5°, mmp 113–114°.

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The Catalytic Methylation of Pyridine and Its Derivatives in the Vapor Phase

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A number of methods have been used to introduce an alkyl group into the pyridine ring. Ladenburg[1] obtained a mixture of 2- and 4-picolines by heating methylpyridinium iodide at 300°. Rieger[2] obtained 2- and 4-picolines by heating pyridine at 80–100° with acetic acid and lead tetraacetate. Propionic acid and lead tetrapropionate gave 2- and 4-ethylpyridine. Goldschmidt and Minsinger[3] heated pyridines with diacyl peroxides and the corresponding acids at 100° and obtained mixtures of 2- and 4-alkylpyridines. 4-Alkylpyridines have been synthesized directly from pyridine by the Wibaut–Arens alkylation[4] which involves the reaction of pyridine with an acid anhydride. Cullinane, *et al.*,[5] passed a mixture of methanol and pyridine vapors over alumina or aluminum silicate catalysts obtaining small yields of 2-, 3-, and 4-picolines and lutidines. Ziegler and Zeiser[6] obtained only 2-butylpyridine by decomposing the addition product of butyllithium and pyridine at 100°. Daniels and Salerni[7] obtained only 2-picoline from the irradiation of diazomethane in pyridine. Recently, Reinecke and Kray[8] have described the α-alkylation of pyridine by heating the base with an alcohol in the presence of W-5 Raney nickel in the liquid phase.

In this paper, we report a convenient method for introducing methyl groups into the pyridine ring by direct reaction with an alcohol or other compound in the vapor phase. Of special significance is the fact that the reaction gives only products substituted in the α positions. The reaction has been applied to pyridine, mono- and disubstituted pyridines, and quinoline.

The method consists of passing a mixture of the pyridine compound and the alkylating agent over a nickel catalyst in the vapor phase. A variety of compounds will serve as methylating agents. A list of those evaluated is found in Table I along with reaction conditions and yields. All of the methylating reagents used gave only substitution on the 2-position with the exception of methanol which gave substitution on both the 2- and 6-positions. This apparently anomalous result may be related to the higher molar ratio of methanol to pyridine than was employed with the other reagents.

The results of a number of experiments on pyridine with different methylating agents are given in Table I.

TABLE I

METHYLATION OF PYRIDINE[a]

Methylating agent	Temp, °C	Mole ratio, methylating agent–pyridine	Contact time, sec	2-Picoline, % yield
Methanol	295	15:1	11.5	57[b]
Ethanol	263	3:1	11.6	61
1-Propanol	300	2.5:1	11.4	52
2-Propanol	295	2.5:1	12.2	38
1-Butanol	298	2.1:1	14.0	48
2-Methyl-1-propanol	298	2.1:1	14.0	25
Acetone	325	2.5:1	12.2	38
Methylal	258	2.3:1	14.0	55
Ethyl orthoformate[c]	256	1.3:1	20.6	57
Ethyl acetate	298	1.6:1	16.2	58
Methane	260	3.8:1	9.8	10
Carbon monoxide–hydrogen	270	2:1:1[d]	11.0	30

[a] Harshaw catalyst Ni-0104T was used in all experiments reported in this table. [b] 2,6-Lutidine formed in 24% yield as coproduct. [c] By-products from this reaction were diethyl ether, carbon monoxide, carbon dioxide, and methane. [d] Mole ratio of H_2–CO–pyridine.

Table II lists results from methylation of substituted pyridines and quinoline with methanol.

TABLE II

ALKYLATION OF PYRIDINE COMPOUNDS WITH METHANOL[a]

Pyridine compd	Temp, °C	Mole ratio, methanol–pyridine compd	Contact, time, sec	Product	Yield, %
2-Picoline	260–265	3.6:1	12.2	2,6-Lutidine	11
3-Picoline	265–269	3.7:1	12.2	2,5-Lutidine	54
4-Picoline	260	3.6:1	11.5	2,4-Lutidine	21
Quinoline	260	4.0:1	13.4	2-Methylquinoline	65
2,4-Lutidine	260	4.0:1	12.2	*s*-Collidine	5

[a] Harshaw catalyst Ni-0104T was used in all experiments reported in this table.

The methylation reactions described in Table II do not proceed in the absence of a nickel catalyst. A study of the behavior of some of the alkylating agents over the catalyst in the absence of pyridine revealed that a fairly large number of gaseous products is formed

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[1] A. Ladenburg, *Ann.*, **247**, 1 (1888).

[2] W. H. Rieger, U. S. Patent 2,502,174 (March 28, 1950).

[3] S. Goldschmidt and M. Minsinger, German Patent 952,807 (Nov. 22, 1956); *Chem. Abstr.*, **53**, 16160 (1959).

[4] J. P. Wibaut and J. F. Arens, *Rec. Trav. Chim.*, **60**, 119 (1941); **61**, 59, (1942).

[5] N. M. Cullinane, S. J. Chard, and R. J. Meatyard, *J. Soc. Chem. Ind.* (London), **67**, 142 (1948).

[6] K. Ziegler and H. Zeiser, *Ber.*, **63**, 1847 (1930).

[7] R. Daniels and O. L. Salerni, *Proc. Chem. Soc.*, 286 (1960)

[8] M. G. Reinecke and L. R. Kray, *J. Am. Chem. Soc.*, **86**, 5355 (1964).

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.

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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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