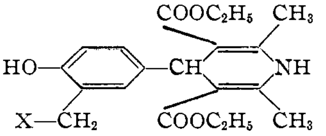
TABLE I

MANNICH BASES FROM A HANTZSCH PYRIDINE SYNTHESIS PRODUCT

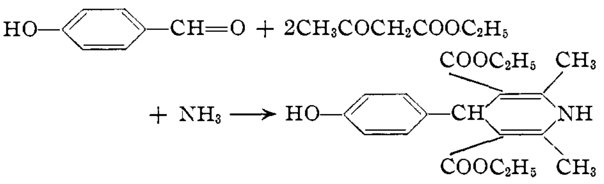


Compd.	X	Yield, %	M.p., °C.[a]	Crystn. solvent[b]	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
I	$(CH_3)_2N$	97	200–205 Sinters 160–200	Æ.H	65.6	65.7	7.5	7.2
II	$(CH_3)_3NI$	40	214–215	M.E.	50.7	51.0	6.1	6.3
III	$(C_2H_5)_2N$	40	157–158	Æ.H	66.9	67.0	8.0	7.6
IV	$(CH_2)_5N$[c]	85	192–193	M	67.8	67.9	7.7	7.6
V	$O(C_2H_4)_2N$[d]	99	182–183	A	64.8	64.8	7.3	7.0

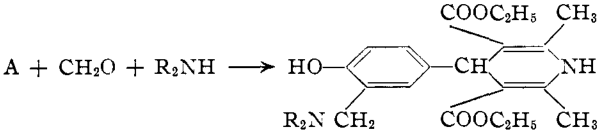
[a] All melting points are uncorrected. [b] A = ethanol; Æ = ethyl acetate; E = ethyl ether; H = hexane; M = methanol. [c] $(CH_2)_5N$ = piperidino. [d] $O(C_2H_4)_2N$ = morpholino.

afforded an alternative type of compound containing a basic side chain.

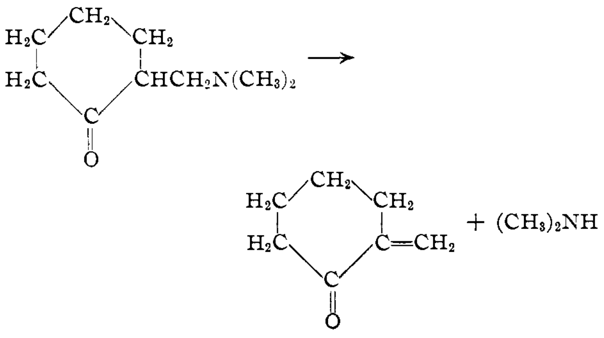
The 2,6-dimethyl-3,5-dicarbethoxy-4-(4′-hydroxyphenyl)-1,4-dihydropyridine (A, see below) was prepared[2] by condensation of *p*-hydroxybenzaldehyde, acetoacetic ester and ammonia. This phenolic dihydropyridine then readily reacted with formaldehyde and secondary amines to give the series of Mannich bases listed in Table I.



A



One of the compounds in Table I (II) is a quaternary methiodide made from I. The poor yield as well as the unfavorable results obtained in attempts to make the corresponding methiodides from one or two of the other Mannich bases suggests that these salts are rather unstable. Although it is well-known that many Mannich bases are relatively unstable, usually these are cases in which by elimination of the elements of the secondary amine an unsaturated compound can result, such as



In the examples described in the present paper some other basis for instability must be considered.

Experimental

Preparation of the Mannich Bases.—A mixture of the 4-(4′-hydroxyphenyl)-dihydropyridine, A (0.02 *M*), formaldehyde (0.022 *M*, as formalin), the secondary amine (0.022 *M*) and 70 cc. of ethanol was heated for four hours on a steam-bath allowing the alcohol to evaporate slowly. After cooling and scratching the oily product gradually crystallized. After purification by recrystallization from the appropriate solvents the results recorded in Table I were obtained.

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Pyrolysis of Perfluoro-*n*-pentane[1]

BY GAIL C. ROGERS AND GEORGE H. CADY

In spite of the fact that the high degree of stability of fluorocarbons is now well known, little specific information regarding either the temperatures required to bring about pyrolysis or the nature of the products formed has been published. This note reports the results of a brief and only partially complete study of the pyrolysis of a single saturated fluorocarbon, perfluoro-*n*-pentane, *n*-C_5F_{12}.

Before the work could be started it was necessary to find a material suitable for the construction of the reaction vessel. Glass and silica offer problems, because at high temperatures they react with fluorocarbons.[2] It was found that both stainless steel and tungsten react rapidly with carbon tetrafluoride at 1000° but that platinum is attacked only very slowly, even at 1500°. With this information at hand a reaction vessel was constructed from a one-liter Pyrex glass flask having at its center a coil wound from a 23 cm. length of 0.0255 cm. diameter platinum wire. During a run, the glass remained cool enough to avoid reaction with the fluorocarbon, while the wire was heated electrically to a desired temperature in the neighborhood of 1000°. Several runs were made to learn the effect of the temperature of the wire upon the reaction. The reaction was followed by the change in pressure of the gas and by measuring the density of the gas. An optical pyrometer was used to

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[2] L. E. Hinkel and W. R. Madel, *J. Chem. Soc.*, 750 (1929).

[1] From the M.S. degree thesis of Gail C. Rogers, 1948.

[2] L. White, Jr., and O. K. Rice, THIS JOURNAL, **69**, 267 (1947).

TABLE I

PYROLYSIS OF n-C_5F_{12}

Temp. Pt filament, °C.	Approx. half time of reaction, min.	Initial pressure C_5F_{12} vapor	Volatile products Moles per mole of C_5F_{12} used					Solid polymer, g./mole of C_5F_{12} used
			CF_4	C_2F_6	C_3F_6	C_3F_6, + C_3F_8	C_4F_8 + higher FC's	
840	∞	150						
900	300	155	0.0	0.0	..	0.4	0.8[a]	12
940	60	262	.0	.2	0.33	.8	.4	5.5
960	12	153	.0	> .14	..	.7	.2	10
1150	3	155	.02	.9	0.38	.6	.2	9
1325	<2	219	.005	1.1	..	.14	.0	37

[a] Most of this material was unreacted C_5F_{12}.

measure the temperature of the filament and it is probable that the temperatures so observed were correct to within about 20°. After the reaction appeared to be complete, the products were identified by making an analytical fractional distillation using a very small fractionating column. Vapor densities and boiling ranges of the different cuts were measured, and in two runs the C_3 cut was chlorinated to permit determination of perfluoropropene. Under these conditions pyrolysis of the fluorocarbon was not detected at 840° and it was slow when the filament was held at 900°. As the temperature was increased above this value the rate became much greater.

The clearly identified reaction products were CF_4, C_2F_6, C_3F_8 and C_3F_6 (perfluoropropene). Evidence was also obtained for the presence of one or more forms of C_4F_8. A high polymer having properties of polytetrafluoroethylene collected on the walls of the flask. A trace of a black material, thought to be free carbon, because it disappeared when heated in air, formed on the hot filament.

Results of the different runs are summarized in Table I. Data regarding rates are too few in number to justify their consideration as a means of determining the order of the reaction. The proportions of the different products as given are not to be regarded as very accurate; however, they do indicate in general the influence of temperature upon the composition of the product.

While the observations do not permit one to draw definite conclusions about the mechanism of the reaction, they do furnish some basis for speculation. The data are in accord with a mechanism in which a molecule of C_5F_{12} may dissociate in either of two ways

$$C_5F_{12} = C_2F_4 + C_3F_8 \qquad (1)$$

$$C_5F_{12} = C_2F_6 + C_3F_6 \qquad (2)$$

If C_2F_4 is formed, it disappears due to rapid polymerization to yield one or more forms of C_4F_8, and $(CF_2)_n$. A part of the perfluoropropene, C_3F_6, may also polymerize. Carbon tetrafluoride may be formed at the higher temperatures due to the decomposition of fluorocarbons resulting from the first steps of the pyrolysis of C_5F_{12}. If reactions 1 and 2 are the primary reactions, it follows that reaction 1 predominates at about 900° and that reaction 2 is the more prevalent at the higher temperatures.

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The Reaction of Benzyl Chloride with n-Heptylmagnesium Bromide[1]

BY ROBERT W. SCHIESSLER, RHOADS M. SPECK[2] AND JOSEPH A. DIXON

The effect of a number of aliphatic Grignard reagents on benzyl chloride and substituted benzyl chlorides at 100° has been studied by Späth.[3] Fair yields of the normal reaction products were obtained. From the reaction of methyl or ethyl Grignard reagents with benzyl chloride, a product later shown[7] to be 1-benzyl-4-(phenylethyl)-benzene was isolated. Miller and Bachman[4] examined the action of phenyl-, n-butyl, n-amyl- and cyclohexylmagnesium bromide and ethylmagnesium iodide on 9-chlorofluorene (a "benzyl" type halide). They found that in ether solution only ethylmagnesium iodide gave an appreciable yield of alkylfluorene. The other Grignard reagents produced 70 to 95% yields of bifluorenyl, in either benzene or ether solution.

Earlier in this Laboratory[5] it was found that the action of n-heptylmagnesium bromide on benzyl chloride produced a high yield of bibenzyl instead of the coupling product, phenyloctane. The present investigation was undertaken to determine other products of the reaction and to gain some understanding of this result, since with allyl bromide and a normal alkyl Grignard reagent the yield of coupling product is usually about 90%.

Benzyl chloride was added to a filtered[6] ether solution of n-heptylmagnesium halide. Aliquots were removed at regular intervals to follow the disappearance rates of the Grignard reagent and halide. Concentrations of the two reactants were determined by an hydrolysis procedure, plots of log concentration of Grignard reagent and benzyl chloride $vs.$ time appear in Fig. 1.

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[1] American Petroleum Institute Project 42. Presented before the Organic Division American Chemical Society, Atlantic City, N. J., 1949.

[2] American Petroleum Institute Research Fellow. Abstracted from an M.S. thesis by Rhoads M. Speck, 1949.

(3) Späth, *Monatsh.*, **34**, 1965 (1913).

(4) Miller and Bachman, THIS JOURNAL, **57**, 766 (1935).

(5) F. B. Fischl and R. W. Schiessler, unpublished data.

(6) See Experimental.