With Allyl Bromide.—A solution of 11.4 g (0.08 mol) of 2-methylpropenylidenebisdimethylamine and 10.9 g (0.09 mol) of allyl bromide in 20 ml of dry acetonitrile was heated to reflux for 3 days. The acetonitrile was evaporated under vacuum to yield 20.5 g (92%) of crude adduct. Recrystallization from acetone gave N,N,N′,N′,2,2-hexamethyl-4-pentenamidinium bromide (**2h**): mp 212–213°; nmr spectrum (in $CDCl_3$), (m) ~4.2, (m) 4.7, (s) 6.52, (d) 7.37, J = 7.0 Hz, (s) 8.37 (1:2:12:2:6).

Anal. Calcd for $C_{11}H_{23}BrN_2$: C, 50.19; H, 8.81; Br, 30.26; N, 10.64. Found: C, 50.23; H, 8.94; Br, 30.13; N, 10.47.

Treatment of 17.1 g of the crude adduct salt with 20 ml of 2 N sodium hydroxide overnight yielded 5.3 g (51% based on 2-methylpropenylidenebisdimethylamine) of N,N,2,2-tetramethyl-4-pentenamide (**3h**): bp 75–80° (4 mm); $n^{25}D$ 1.4641; nmr spectrum (in CCl_4), (m) ~4.2, (m) ~5.0, (s) 6.99, (d) 7.64, J = 7.0 Hz, (s) 8.78 (1:2:6:2:6).

Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02; mol wt, 155. Found: C, 69.53; H, 10.96; N, 9.16; mol wt, 155.

With Butyl Iodide.—A mixture of 8.5 g (0.06 mol) of 2-methylpropenylidenebisdimethylamine, 11.1 g (0.06 mol) of butyl iodide, and 20 ml of acetonitrile was heated to reflux for 11 days. The acetonitrile was removed under vacuum to give 15.2 g of yellow semisolid. Recrystallization afforded 0.5 g of crude N,N,-N′,N′,2-pentamethylpropionamidinium iodide, whose nmr spectrum was identical with that of the bromide prepared by addition of dry hydrogen bromide to 2-methylpropenylidenebisdimethylamine. The bulk of the crude product could not be induced to crystallize. The crude product was dissolved in 15 ml of 2 N sodium hydroxide and allowed to stand overnight. The mixture was extracted with ether and the extract distilled to obtain 1.8 g (18%) of N,N,2,2-tetramethylhexanamide (**3j**): bp 61–62° (0.7 mm); $n^{25}D$ 1.4512; nmr spectrum (in CCl_4), (s) 7.02, (s) 8.81, (m) 8.70, (m) 9.05 (2:2:2:1).

Anal. Calcd for $C_{10}H_{21}NO$: C, 70.12; H, 12.36; N, 8.18; mol wt, 171. Found: 69.92; H, 12.28; N, 8.18; mol wt, 171.

The aqueous layer remaining after ether extraction was filtered and the crystals so obtained were recrystallized from acetone–tetrahydrofuran to yield 0.6 g (5.4% yield based on 2-methylpropenylidenebisdimethylamine) of material identified as 3-dimethylamino-N,N,N′,N′,2,2,4-heptamethyl-3-pentenamidinium iodide (**6**, X = I): mp 189–191° dec; nmr spectrum (in $CDCl_3$), (s) 6.58, (s) 7.27, (s) 8.30, (s) 8.40, (s) 8.49 (4:2:1:2:1).

Anal. Calcd for $C_{14}H_{30}IN_3$: C, 45.78; H, 8.23; I, 34.55; N, 11.44. Found: C, 45.64; H, 8.27; I, 34.81; N, 11.28.

When butyl bromide was used in place of the iodide, 17 days were required for complete disappearance of the reactants. A total of 15.4 g (69%) of N,N,N′,N′,2-pentamethylpropionamidinium bromide, mp 263° dec, was recovered by crystallization from the reaction mixture. The nmr spectrum was identical with that of an authentic sample of the salt, mp 267° dec, prepared by addition of dry hydrogen bromide to 2-methylpropenylidenebisdimethylamine: mmp 266° dec; nmr spectrum (in CH_2Cl_2), (m) ~6.4, (s) 6.58, (d) 8.53, J = 7.2 Hz (12:6:1).

Anal. Calcd for $C_8H_{19}BrN_2$: C, 43.05; H, 8.58; Br, 35.81; N, 12.55. Found: C, 42.94; H, 8.67; Br, 35.94; N, 12.42.

The remainder of the reaction mixture was hydrolyzed in 2 N sodium hydroxide. Extraction with ether, followed by distillation of the extract, afforded less than 1% yield of crude N,N,2,2-tetramethylhexanamide.

Registry No.—N,N,N′,N′-Tetramethyl-3-phenylpropionamidinium hexafluorophosphate, 12260-64-9; 3-phenylpropenylidenebisdimethylamine, 16487-48-2; **2c,** 16487-49-3; **2d,** 16520-61-9; **2e,** 16487-50-6; **2f,** 16487-51-7; **2g,** 16487-52-8; **2h,** 16487-53-9; **3e,** 5830-31-9; **3f,** 16487-55-1; **3g,** 16487-56-2; **3h,** 16487-57-3; **3i,** 5830-30-8; **3j,** 16487-59-5; **6** (X = PF_6), 12260-65-0; **6** (X = I), 16487-60-8; dibenzyldimethylammonium hexafluorophosphate, 12260-70-7; N,N,N′,N′,2-pentamethylpropionamidinium bromide, 16487-61-9.

Acknowledgment.—The authors thank Mrs. Nancy K. Edelmann for nmr analyses and for preparation of intermediates.

Reductive Alkylation of Imines and Esters with Sodium in Ammonia

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Diphenyl- or pyridylketimines and pyridylaldimines were alkylated at carbon by the addition of sodium metal in liquid ammonia, followed by an organic halide. The same products were obtained by treating the corresponding amine with sodamide in liquid ammonia, followed by the halide. Similar reductive alkylations of methyl isonicotinate with benzyl chlorides gave the corresponding 4-pyridyl ketones.

Numerous reactions in organic synthesis involve the alkylation of carbanions. One route to such intermediates is the addition of electrons from alkali metals to an unsaturated center. The addition of the first electron gives a radical anion, which in the case of most double bonds is so reactive that it dimerizes or reacts with the solvent. In some instances, however, a second electron can be added to give a stable dianion. Schlenk[1] was first to show that a relatively stable dianion can be formed by treating diaryl ketones with sodium in ether and that this dianion can be alkylated with ethyl or methyl iodides. Later workers[2] showed that the dianions, formed from diaryl ketones with sodium in liquid ammonia, alkylated preferentially at carbon with a variety of alkylating agents, but aryl alkyl or dialkyl ketones would not alkylate under these conditions.

$$Ar_2C{=}O \xrightarrow[NH_3]{2Na} \left[Ar_2\overset{\ominus}{C}{-}\overset{\ominus}{O}\right]2Na^{\oplus} \xrightarrow{RX} Ar_2\underset{R}{\underset{|}{C}}{-}O^{\ominus}Na^{\oplus}$$

Kharasch[3] studied the reductive alkylation of esters and obtained 30–35% yields of ketones from the following esters and alkyl halides.

$$RCOOC_2H_5 \xrightarrow[NH_3]{2Na} \left[RC(=O)^{\ominus}\right]Na^{+} \xrightarrow{R'Br} RC(=O)R'$$

R = C_6H_5, *i*-Pr, *t*-Bu; R′ = *n*-Bu, Et

However, with benzyl chloride and ethyl benzoate, only a 5% yield of ketone was detected.

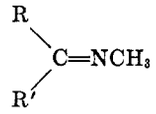
(1) W. Schlenk and T. Weikel, *Chem. Ber.*, **44**, 1182 (1911).

(2) (a) P. J. Hamrick and C. R. Hauser, *J. Amer. Chem. Soc.*, **81**, 493 (1959); (b) D. V. Ioffe, *Zh. Obshch. Khim.*, **34**, 703 (1964); **35**, 1851 (1965); (c) E. L. Anderson and J. E. Casey, Jr., *J. Org. Chem.*, **30**, 3960 (1965); (d) S. Selman and J. Eastham, *ibid.*, **30**, 3804 (1965); (e) J. A. Gautier, M. Miocque, C. Fauran, and M. D. D'Engenieres, *Bull. Soc. Chim. Fr.*, 3762 (1965).

(3) M. S. Kharasch, E. Sternfeld, and F. Mayo, *J. Org. Chem.*, **15**, 362 (1940).

TABLE I

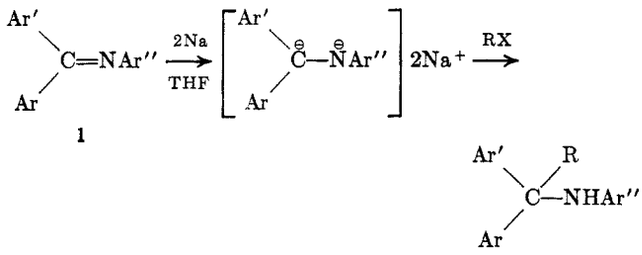
N-METHYLIMINES



No.	R	R′	Bp (mm) or mp, °C	Yield, %	Reaction conditions[a]	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
2a	C_6H_5	H[b]	183–185 (atm)	61	A, 15 hr, 25°	C_8H_9N	...	...	...	...	...	...
2b	C_6H_5	CH_3[c]	206–208 (atm)	82	B, 19 hr, 120°	$C_9H_{11}N$	...	...	...	...	...	...
2c	C_6H_5	C_6H_5[d]	147–148 (3.0)	97	B, 18 hr, 125°	$C_{14}H_{13}N$	86.12	6.71	7.17	86.24	6.65	7.13
2d	2-C_5H_4N	H	67–70 (8.0)	93	C, 2 hr, 25°	$C_7H_8N_2$	69.97	6.71	23.32	70.22	6.83	23.61
2e	3-C_5H_4N	H	70–75 (10.0)	91	C, 2 hr, 25°	$C_7H_8N_2$	69.97	6.71	23.32	69.98	6.98	23.30
2f	4-C_5H_4N	H	70–75 (10.0)	90	C, 2 hr, 25°	$C_7H_8N_2$	69.97	6.71	23.32	70.29	6.99	23.51
2g	2-C_5H_4N	CH_3	108–110 (30)	86	B, 5 hr, 90°	$C_8H_{10}N_2$	71.61	7.51	20.88	71.57	7.26	21.02
2h	3-C_5H_4N	CH_3	123–124 (20)	61	B, 24 hr, 120°	$C_8H_{10}N_2$	71.61	7.51	20.88	71.91	7.41	20.93
2i	4-C_5H_4N	CH_3	123–127 (20)	85	B, 6 hr, 95°	$C_8H_{10}N_2$	71.61	7.51	20.88	71.15	7.55	21.08
2j	4-C_5H_4N	C_6H_5	120–125 (0.2)	67	B, 8 hr, 90°	$C_{13}H_{12}N_2$	*e*					
2k	4-$O_2NC_6H_4$	H	105–107[f]	78	A, 1 hr, 60°	$C_8H_8N_2O_2$	...	...	...	...	...	...

[a] A, aqueous methylamine; B, liquid methylamine as solvent; C, methylamine in benzene. [b] N. Cromwell, R. Babson, and C. Harris, *J. Amer. Chem. Soc.*, **65**, 313 (1943). [c] W. Saunders and E. A. Caress, *ibid.*, **86**, 861 (1964). [d] C. Hauser, R. Manyik, W. Brasen, and P. Bayless, *J. Org. Chem.*, **20**, 1119 (1955). [e] Gas chromatography showed product to be 97% pure. [f] A. Burawoy and J. Critchley [*Tetrahedron*, **5**, 340 (1959)] reported mp 106°.

In the case of carbon–nitrogen double bonds, only N-arylimines of type **1** have been studied to date.[4] The latest paper by Smith and Veach establishes that carbon alkylation is the exclusive product with monohalides.



1

Gautier[5] recently showed that oximes derived from diaryl ketones, treated with 4 mol of sodium in ammonia followed by an organic halide, underwent reductive alkylation at carbon, giving good yields of amines.

Our investigation concerned the use of alkyl and unsubstituted imines in the reductive alkylation reaction (Scheme I).

Diaryl ketones readily give the dianion with sodium in liquid ammonia, but with imines one would not expect **3** to predominate if R″ is not aryl. Since anions of secondary and primary amines are of comparable basicity to the NH_2^- ion, the large excess of ammonia would insure a low concentration of **3** or **5**. Whether the predominant species is **4** or **6** clearly depends on the substituents, R and R′.

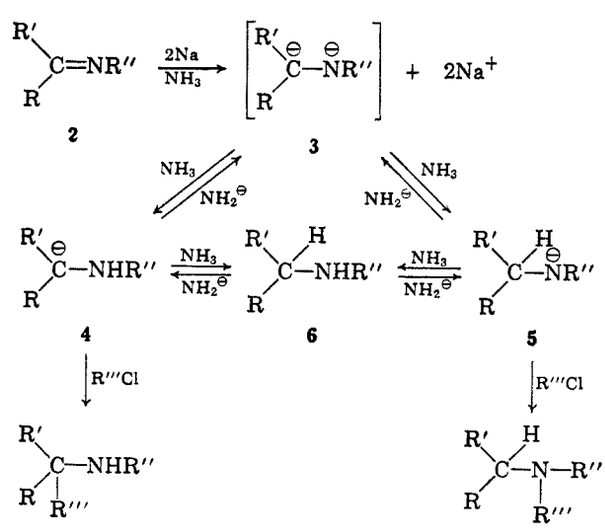
Results and Discussion

Preparation of Imines.—The N-methylimines were conveniently prepared by the reaction of the corresponding carbonyl compound with an excess of anhydrous methylamine. With aldehydes, the reaction was exothermic, but with aryl ketones, heating in an autoclave was necessary. Conditions and results are summarized in Table I.

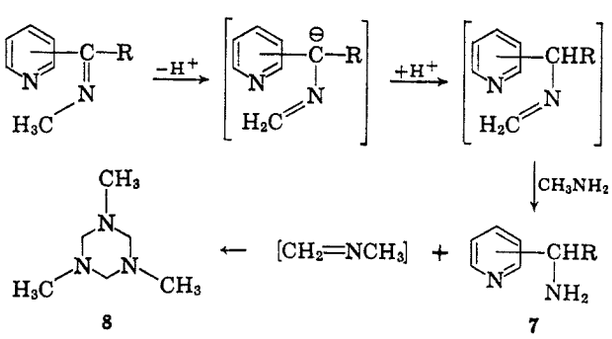
(4) (a) W. Schlenk and E. Bergmann, *Ann. Chem.*, **463**, 281 (1928); (b) B. M. Mikhailov and K. Kurdiumova, *J. Gen. Chem. USSR*, **25**, 1687 (1955); (c) J. G. Smith and C. D. Veach, *Can. J. Chem.*, **44**, 2245 (1966).

(5) J. A. Gautier, M. Miocque, C. Fauran, and A. Y. Cloarec, *Compt. Rend.*, **263**, 1164 (1966).

SCHEME I



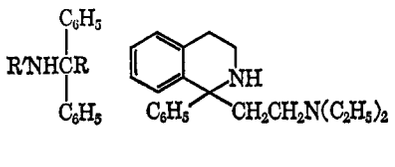
For the preparation of some of the pyridylketimines, the indicated reaction conditions are critical. Milder conditions gave unreacted ketone, and more vigorous conditions led to the production of the hydrotriazine (**8**) and the primary amine **7**. Their formation can be rationalized by the following sequence.



This side reaction is most serious in the 2-pyridyl, less so in the 4-pyridyl, and not detected at all in the 3-pyridyl series. With **7** (R = CH_3) the triazine **8** distilled at the same temperature as **7**, but with **7** (R = C_6H_5) they were easily separated. This per-

TABLE II

PRODUCTS FROM THE REDUCTIVE ALKYLATION OF IMINES WITH SODIUM AND ALKYL CHLORIDES[a]



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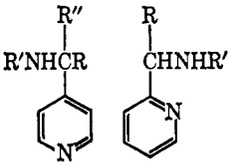

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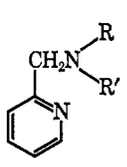

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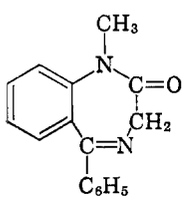
No.	R, R′, R″	Yield, %	Mp or bp (mm), °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
16a	$(C_2H_5)_2NCH_2CH_2$, H	78[b]	144–148 (0.5)[c]	$C_{19}H_{26}N_2$	80.80	9.28	9.92	80.67	9.16	9.98
16b	$(CH_3)_2NCH_2CH_2$, H	71	75–84[d]	$C_{17}H_{22}N_2$	80.27	8.72	11.01	80.18	8.67	10.99
16c	$(C_2H_5)_2NCH_2CH_2$, CH_3	70	69–70	$C_{20}H_{28}N_2$	81.03	9.25	9.45	81.11	9.60	9.31
16d	$HC{\equiv}CCH_2$, H	48	248–251[e]	$C_{16}H_{16}ClN$	74.20	6.22	5.43	74.37	6.24	5.61
16e	H, $(CH_3)_3Si$[f]	57	105–110 (0.1)	$C_{16}H_{21}NSi$	75.26	8.29	5.49	75.31	8.14	5.55
17		69	155–158 (0.3)	$C_{21}H_{28}N_2$	81.71	9.15	9.08	81.76	8.99	9.17
18a	$(C_2H_5)_2NCH_2CH_2$, CH_3, H	42	110–112 (0.3)	$C_{13}H_{23}N_3$	70.54	10.47	18.98	70.58	10.68	19.19
18b	$HC{\equiv}CCH_2$, CH_3 H	29	200–202[g]	$C_{10}H_{14}Cl_2N_2$	51.50	6.01	12.01	51.24	6.04	11.93
18c	$C_6H_5CH_2$, CH_3, H	50[h]	248–251[i]	$C_{14}H_{18}Cl_2N_2$	59.00	6.36	9.84	58.71	6.15	9.79
18d	4-$ClC_6H_4CH_2$, CH_3, H	11	260–263[j]	$C_{14}H_{17}Cl_3N_2$	52.40	5.37	8.98	52.31	5.49	9.18
18e	$(C_2H_5)_2NCH_2CH_2$, CH_3, CH_3	60	110–115 (0.2)	$C_{14}H_{25}N_3$	71.44	10.71	17.85	71.59	10.70	17.91
18f	$C_6H_5CH_2$, CH_3, CH_3	22	235–238[k]	$C_{15}H_{20}Cl_2N_2$	60.40	6.73	9.37	60.25	6.90	9.57
19a and 20	$(C_2H_5)_2NCH_2CH_2$, CH_3	24[l]	112–115 (0.8)	$C_{13}H_{23}N_3$	70.54	10.47	18.98	70.46	10.74	19.12

[a] All reactions were conducted in liquid ammonia unless otherwise specified. [b] Also carried out in DME giving a 54% yield. [c] Dihydrochloride, mp 268–269° (lit.[5] mp 251°). [d] Lit.[5] mp 75°. [e] Melting point of hydrochloride; free base, bp 118–123 (0.3 mm) (ref 5 reports melting point of maleate at 190°). [f] DME solvent. [g] Melting point of hydrochloride; free base, bp 78–80 (0.1 mm). [h] Yield by glpc; yield of pure salt 33%. [i] Melting point of hydrochloride; free base, bp 120–125° (0.2 mm). [j] Melting point of hydrochloride; free base, bp 130–135° (0.2 mm). [k] Melting point of hydrochloride; free base, bp 150–160 (0.2 mm). [l] Composed of 71% **20** and 29% **19a**.

mitted the isolation of **7** (2- and 4-pyridyl, R = C_6H_5) in good yield when the appropriate reaction conditions were used (see Experimental Section).

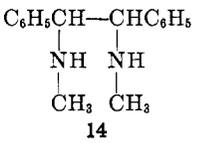
It is also interesting to note that while benzophenone gave a methylimine in excellent yield, dibenzo[*a*,*d*]cycloheptan-5-one failed to react appreciably (only 10% conversion) with methylamine even under more vigorous conditions (150°, 2 days). In contrast, fluorenone reacted readily, but the nmr spectrum of the product revealed a complex mixture of products, including the type of reaction encountered in the pyridine series. Ammonia, however, reacts normally to give fluoren-9-onimine (**9**).[6]

The following were prepared as starting materials by literature methods: **9**,[6] diphenylketimine (**10**),[7] 1-phenyl-3,4-dihydroisoquinoline (**11**),[8] and **12**.[9]



12

Reductive Alkylation.—Imines of type **2**, where R = R′ = C_6H_5 or R = 4-pyridyl, R′ = H, CH_3, or C_6H_5, and the cyclic imine **11** underwent reductive alkylation at carbon, using sodium in ammonia and a variety of organic chlorides. Good yields of amines **16**, **17**, and **18** were obtained (see Table II). When R was 3-pyridyl, only polymeric material was formed with 2-diethylaminoethyl chloride (**13**) as the alkylating agent. When R was 2-pyridyl, reductive alkylation with **13** gave tars plus a mixture of C- and N-alkylated amine, with N-alkylation predominating (70:30). With the methylimine from benzaldehyde no alkylation occurred. Only N-methylbenzylamine and the dimer **14** were isolated (presumably from radical ion intermediate). From the methylimine of acetophenone, only the reduced product resulted. Other starting materials which failed to give pure alkylated products were compounds **2h** (Table I), **9**, and **12**, as well as isoquinoline, acridine, and benzonitrile. Attempts to use dihalides to synthesize aziridines and azetidines of type **15** also were unsuccessful.



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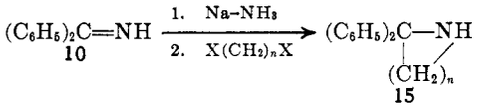


15

Using sodium dispersion in 1,2-dimethoxyethane (DME), **10** gave the same C-alkylated product with **13** as it did in ammonia but in lower yield. Trimethylsilyl chloride (which is too reactive for use in ammonia) reacted with the sodium adduct of **10** in DME to give the N-alkylated product, presumably because of steric hindrance to C-alkylation. Since DME is aprotic, it seems likely that the disodio derivative **3** (R = R′ = C_6H_5, R″ = H) is the predominant species present in this solvent. Results of all successful reductive alkylations are summarized in Table II.

(6) L. Pinck and G. Hilbert, *J. Amer. Chem. Soc.*, **56**, 490 (1934).
(7) Moureu and Mignonac, *Compt. Rend.*, **56**, 1806 (1913).
(8) W. Whaley and W. Hartung, *J. Org. Chem.*, **14**, 650 (1949).
(9) L. H. Sternbach, R. I. Fryer, W. Metlesics, E. Reeder, S. Sach, G. Sancy, and A. Stempel, *ibid.*, **27**, 3788 (1962).

TABLE III

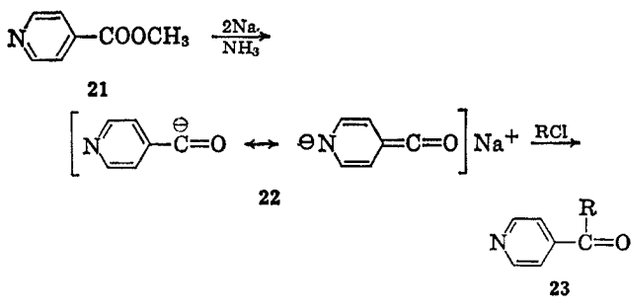
PRODUCTS FROM ALKYLATION OF AMINES WITH ALKYL CHLORIDES (RCl) USING SODIUM AMIDE IN LIQUID AMMONIA

No.[a]	R, R', R''	Yield, %	Mp or bp (mm), °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
16a	$(C_2H_5)_2NCH_2CH_2$, H	77	See Table II							
18c	$C_6H_5CH_2$, CH_3, H	57	See Table II							
19a and 20	$(C_2H_5)_2NCH_2CH_2$, CH_3	63[b]	See Table II 155–158 (0.1)							
18g	$(C_2H_5)_2NCH_2CH_2$, CH_3, C_6H_5	45	56–58	$C_{19}H_{27}N_3$	76.72	9.15	14.13	76.80	9.16	14.03
18h	$(C_2H_5)_2NCH_2CH_2$, H, H	54	205–210[c]	$C_{12}H_{24}Cl_3N_3$	45.53	7.63	13.26	43.26[d]	7.75	13.17
19b	$(C_2H_5)_2NCH_2CH_2$, H	55	120–122 (0.7)	$C_{12}H_{21}N_3$	69.52	10.21	20.27	69.44	10.22	20.43
19c	$HC{\equiv}CCH_2$, H	12	72–75 (0.5)	$C_9H_{10}N_2$	73.94	6.89	19.16	74.16	6.99	19.36
19d	$C_6H_5CH_2$, H	18	238–240[e]	$C_{13}H_{16}Cl_2N_2$	57.65	5.95	10.34	57.61	6.00	10.43

[a] See Table II for structures. [b] Composed of 52% **20** and 48% **19a**. [c] Melting point of trihydrochloride; free base, bp 118–125° (0.3 mm). [d] *Anal.* Calcd for Cl: 33.35%. Found: 33.77%. [e] Melting point of dihydrochloride; free base, bp 130–135° (0.8 mm).

These results indicate that reductive alkylation occurs with only those imines, which, upon addition of sodium in liquid ammonia, afford carbanions that are weaker bases than sodium amide. One should then be able to get the same intermediates by treating the reduced imine (*i.e.*, the amine) with sodium amide in liquid ammonia. Subsequent alkylation would give identical products. This proved to be the case. Benzhydrylamine with sodium amide (1.3 mol) in liquid ammonia gave a dark red solution, also formed from the imine **10** when it was added to a sodium–ammonia solution. Alkylation with diethylaminoethyl chloride (**13**) gave the same product, **16a**, in comparable yield. This comparison also was extended to 4-pyridine aldehyde methylimine and its corresponding amine, using benzyl chloride as the alkylating agent. The same product, **18c**, resulted, and gas chromatography of the crude product showed it was contaminated with even the same impurities. However, comparison of 2-pyridine aldehyde methylimine and the corresponding amine, showed significant differences in the reaction with **13**. N-Alkylation predominated in both cases but the sodium amide method gave a higher yield (63 *vs.* 24%) of a mixture containing a higher proportion (48 *vs.* 29%) of the C-alkylated isomer. A number of sodium amide alkylations using 2- and 4-aminomethylpyridines were carried out and are summarized in Table III. With 2-aminomethylpyridine, only C-alkylation was observed while its N-methyl derivative gave 52% N-alkylation. One would have to know more about the relative acidities and reactivities of the carbanions and nitranions derived from them to explain these results.

In view of our promising results with 2- and 4-pyridylimines and Kharasch's[3] fair success in the reductive alkylation of simple esters, extension of the reactions to pyridyl esters seemed to be in order. Hopefully, Kharasch's supposed intermediate would acquire more resonance stabilization (*e.g.*, **22**) in the pyridine system.



21

22

23

Reductive alkylation of **21** with benzyl- and *p*-chlorobenzyl chlorides gave 54 and 34% yields of **23** respectively. This is much better than Kharasch's 5% with benzyl chloride and ethyl benzoate. However, ethyl bromide, diethylaminoethyl chloride (**13**), and allyl chloride failed to give significant yields of ketone with **21**. Methyl picolinate also was used but, even with benzyl chloride, failed to give any benzyl 2-pyridyl ketone. It was suspected that benzyl sodium may be the reactive intermediate instead of **22** in the successful runs, but reversing the order of addition (adding the benzyl chloride to the sodium in ammonia, followed by the ester) gave only bibenzyl and no ketone in these cases.

Experimental Section

All compounds gave infrared and nmr spectra consistent with their assigned structures.

Preparation of N-Methylimines (2).—The conditions for the preparation of N-methylimines are listed in Table I. For aldehyde imines, 3 equiv of methylamine in the solvent listed were used for each equivalent of aldehyde. For the other imines, 0.2 mol of ketone was dissolved in 100 ml of liquid methylamine and heated in an autoclave at the temperature and for the time listed in the table. The methylamine was vented, and the residue was dissolved in ether, dried over potassium carbonate, and distilled.

4-(α-Methylaminobenzyl)pyridine (18, R = H; R' = CH_3; R'' = C_6H_5).—The imine **21** (82.5 g) was hydrogenated in ethanol at 40 psi using a 5% platinum–charcoal catalyst. Distillation gave 68.0 g (82%) of product, bp 130–135° (0.2 mm). A small amount of higher boiling material was recovered which contained phenyl-4-pyridylmethanol. Treatment of the base with excess alcoholic hydrogen chloride gave the dihydrochloride, mp 238–240°.

Anal. Calcd for $C_{13}H_{16}Cl_2N_2$: C, 57.51; H, 5.91; N, 10.32. Found: C, 57.71; H, 6.10; N, 10.64.

4-α-Aminobenzylpyridine (18, R = C_6H_5; R' = R'' = H).—4-Benzoylpyridine (55.0 g) was dissolved in 300 ml of methylamine and heated for 30 hr at 150° in an autoclave. The autoclave was cooled and vented. The residue was taken up in ether, dried over potassium carbonate, and distilled to give 3.40 g, bp 50–60° (0.8 mm), and 45.8 g, bp 130–140° (0.2 mm). The low boiling fraction was redistilled to give 2.52 g, bp 75–80° (10 mm). Its nmr spectrum showed it to be the triazine *8*.

Anal. Calcd for $C_6H_{15}N_3$: C, 55.78; H, 11.70; N, 32.52. Found: C, 55.83; H, 11.76; N, 32.73.

Gas chromatography of the higher boiling fraction indicated the presence of 67% of the primary amine **18** and 24% of the N-methylimine **2j**. (*Note:* Running the reaction for a longer period of time did not lower the percentage of **2j**.) The dihydrochloride was prepared with hydrogen chloride in 2-propanol. After two recrystallizations from ethanol–2-propanol, there was obtained 42.3 g (56%) of dihydrochloride, mp 231–234° (lit.[10] mp 234–236°).

(10) C. Lovell and K. Rorig, U. S. Patent 3,025,302 (1962); *Chem. Abstr.*, **57**, 11173*b*,*c* (1962).

2-α-Aminobenzylpyridine (19, R = C_6H_5; R′ = H).—2-Benzoylpyridine (55.0 g) was treated as in the foregoing procedure for 24 hr at 130°. The product [24.5 g, 45% yield, bp 135–140° (0.2 mm)] was at least 90% pure as indicated by nmr analysis. The dihydrochloride melted at 242–244° (lit.[11] mp 242–244°).

Reductive Alkylation with Sodium in Ammonia.—To 300 ml of liquid ammonia under a nitrogen atmosphere, and cooled in a Dry Ice–acetone bath, was added 5.17 g of sodium (0.225 g-atom). After all the sodium had dissolved (blue-black solution), a solution of 0.10 mol of the imine in 25 ml of dry ether was added dropwise over a 15-min period. This was stirred for 15 min, and then a solution of 0.11 mol of the halide in 25 ml of ether was added over another 15-min period. The dark-colored solution was stirred for 3–4 hr at the Dry Ice bath temperature under a nitrogen atmosphere. Then 10 ml of water was added slowly, the ammonia was evaporated on a warm water bath, and the residue was taken up in ether and 25 ml of water. The ether layer was separated and dried over anhydrous potassium carbonate. Removal of the drying agent by filtration and distillation of the filtrate gave the products listed in Table II.

1,2-Diphenyl-N,N′-dimethylethylenediamine (14).—When benzaldehyde methylimine was subjected to the foregoing conditions using diethylaminoethyl chloride as the alkylating agent, the color of the solution changed from blue-black to light yellow after less than half of the halide had been added. The mixture was worked up in the prescribed way to give N-methylbenzylamine and a 45% yield of **14** as a mixture of *meso* and *dl* isomers. The isomers could be partially separated into the solid *meso*, mp 115–124° (lit.[12] mp 135°) and the liquid *dl* form. The nmr spectra indicated that the liquid contained very little *meso*, and the solid contained about 80% *meso* form. The liquid was the major (80%) product in the mixture.

Anal. (for liquid *dl*). Calcd for $C_{16}H_{20}N_2$: C, 79.83; H, 8.37. Found: C, 79.96; H, 8.39.

Use of Dimethoxyethane (DME) Solvent. N-Trimethylsilylbenzhydrylamine (16e).—To a suspension of 3.90 g of sodium dispersion in 110 ml of DME was added, dropwise with stirring in a nitrogen atmosphere, a solution of 9.0 g of diphenylketimine (10) in 30 ml of DME. A dark blue solution formed. After being stirred for 0.5 hr, the solution was cooled to −30° and 7.0 g of trimethylsilyl chloride dissolved in 30 ml of DME was added over a 15-min period. At the end of the addition the reaction mixture changed to a light pink color but on warming to room temperature it became dark red. Water (10 ml) was added to discharge the color, the DME was removed under reduced pressure, and the residue was treated with ether and water. The ether layer was separated, dried, and distilled. See Table II for the results.

Benzyl 4-Pyridyl Ketone (23, R = $C_6H_5CH_2$).—A solution of methyl isonicotinate (20.0 g) in 50 ml of ether was added over a 15-min period to a solution of 6.90 g of sodium in 250 ml of liquid ammonia kept under a nitrogen atmosphere and cooled in a Dry Ice–acetone bath. This was stirred for 5 min, and then 19.0 g of benzyl chloride dissolved in 40 ml of ether was added over a 20-min period. The Dry Ice–acetone bath was removed, and the mixture was stirred for 1.3 hr. Water (100 ml) was added slowly, the ammonia was evaporated on a warm water bath, and the residue was extracted with ether (50 ml) and then with chloroform (250 ml). (*Note*: The color of the solution changed from black to yellow on addition of chloroform.) Drying and removing the chloroform by distillation gave 15.6 g (54%) of ketone, mp 94–96° (chloroform–ether) (lit.[13] mp 96°). From the ether extract no ketone was obtainable.

***p*-Chlorobenzyl 4-Pyridyl Ketone** (23, R = 4-$ClC_6H_4CH_2$).—Substituting *p*-chlorobenzyl chloride for benzyl chloride in the foregoing procedure gave a 42% yield of the chloro ketone, mp 85–87° (chloroform—ether).

Anal. Calcd for $C_{13}H_{10}ClNO$: C, 67.50; H, 4.35; N, 6.06. Found: C, 67.30; H, 4.38; N, 6.24.

Sodium Amide Alkylations.—To a suspension of 11.5 g (0.13 mol) of sodium amide in 300 ml of ammonia at −33° was added 0.10 mol of the amine. After being stirred for 20 min, the dark red solution was cooled in a Dry Ice–acetone bath. Then, under nitrogen, 0.10 mol of the halide dissolved in 30 ml of dry ether was added over a 15-min period. The reaction mixture was treated as specified above for the reductive alkylation. An exception was in the alkylation of 4-(α-methylaminobenzyl)pyridine. Here the reaction mixture was kept overnight in an autoclave at 15° instead of for 4 hr at −60°. Data are summarized in Table III.

Registry No.—**2d**, 7032-20-4; **2e**, 16273-54-4; **2f**, 16273-55-5; **2g**, 16273-56-6; **2h**, 16273-57-7; **2i**, 16273-58-8; **2j**, 16273-59-9; **16a**, 16273-85-1; **16c**, 16273-60-2; **16d**, 16273-61-3; **16d**·HCl, 16273-62-4; **16e**, 16273-86-2; **17**, 16273-63-5; **18a**, 16273-64-6; **18b**, 16273-65-7; **18b**·HCl, 16273-66-8; **18c**, 16273-67-9; **18c**·HCl, 16273-68-0; **18d**, 16273-69-1; **18d**·HCl, 16273-70-4; **18e**, 16273-71-5; **18f**, 16273-72-6; **18f**·HCl, 16273-73-7; **18g**, 16273-74-8; **18h**, 16273-75-9; **18h**·HCl, 16273-76-0; **18**(R = H; R′ = CH_3; R″ = C_6H_5)·2HCl, 16273-77-1; **19a**, 16273-78-2; **19b**, 16273-79-3; **19c**, 16273-80-6; **19d**, 16273-81-7; **19d**·2HCl, 16273-82-8; **20**, 16273-83-9; **23**, 16273-84-0; sodium, 7440-23-5; ammonia, 7664-41-7.

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