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Reaction of Secondary and Tertiary Aldehydes with Ammonia

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The "hydroamide" structure of "triisobutylidenediamine," first prepared by Lipp from isobutyraldehyde and ammonia, has been confirmed. Compounds having this same type of structure are produced by the reaction of tertiary aldehydes and ammonia. The hydroamides of secondary aldehydes are thermally decomposed to *N*-alkylidenealkenylamines; the corresponding derivatives of tertiary aldehydes are dissociated to nitriles and aldimines.

It is generally considered that lower aliphatic aldehydes react with ammonia to first form simple addition compounds, called "aldehyde ammonias." These unstable compounds are easily decomposed to the original constituents, or they may lose water to form imines, which polymerize to trimers and complex amorphous products.[1] These generalizations may be valid for primary aldehydes, RCH_2-CHO, but the behavior of secondary aldehydes, R_2CHCHO, with ammonia follows a different course. Lipp treated isobutyraldehyde with aqueous ammonia solution and obtained an unstable crystalline product, which decomposed readily on heating to "triisobutylidenediamine" (I).[2] The structure assignment for I was analogous to that of an aromatic "hydroamide" (III). Unlike III, which is converted by prolonged heating to a 2,4,5-triaryldihydroimidazole (IV),[3] I was decomposed during a slow distillation to *N*-isobutylidene-2-methylpropenylamine (II). The direct synthesis of homologs of II from aldehydes and ammonia has been claimed as a general method, applicable to secondary aldehydes containing at least five carbon atoms.[4]

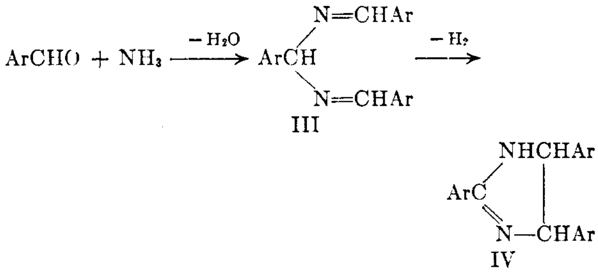
$$(CH_3)_2CHCHO + NH_3 \longrightarrow (CH_3)_2CHCH[N{=}CHCH(CH_3)_2]_2 + H_2O$$

I

$$\downarrow$$

$$(CH_3)_2C{=}CHN{=}CHCH(CH_3)_2 + NH_3$$

II



III

IV

We reviewed Lipp's work with isobutyraldehyde and ammonia and obtained I by rapid distillation of the reaction mixture under reduced pressure. The presence of unstable intermediate condensation products was indicated by some decomposition during the early stages of the distillation. The hydroamide structure of I was confirmed by elemental analysis, molecular weight, and infrared and NMR spectra. The infrared spectrum showed strong bands characteristic of C=N but an absence of any absorption characteristic of —OH and $-NH_2$. The NMR spectrum (Fig. 1) had significant peaks at −96 (a), 33 (b), 111 (c), and 154 c.p.s. (d). Approximate areas under the peaks relative to (b) were (a) 2, (b) 1, (c) 3, and (d) 18. The four peaks in the methyl resonance region (d) were two doublets of relative intensities 2:1. The weaker doublet at the right in Fig. 1 was overlapped by the stronger one to give the closely spaced structure at the center. The doublets themselves arise from spin-spin interaction of a single proton with methyl groups, as in an isopropyl group. Relative intensities of these doublets indicated four equivalent methyl groups distinct from two other equivalent methyl groups. Structure I satisfied these conditions. The peaks at (c) were believed to arise from the three tertiary protons of the isopropyl groups, but multiple splitting precluded their differentiation. The peaks at (b) were in a logical position for the structure $=N-\overset{|}{C}H-N=$, where the proton is in the presence of two electronegative nitrogen atoms. The peaks at (a) were expected for the two —CH=N— groupings; other compounds with this linkage, studied in these laboratories, have exhibited peaks at about −100 c.p.s. The quadruplet structure at

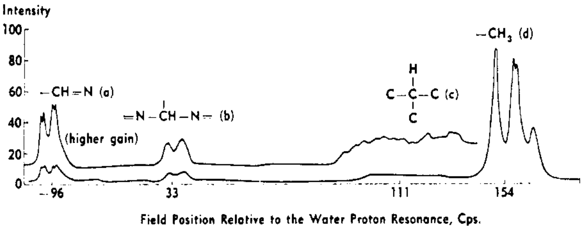


Fig. 1. NMR spectrum of "triisobutylidenediamine" (I)

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[1] M. M. Sprung, *Chem. Revs.*, 26, 301 (1940).

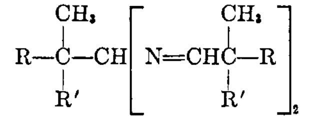
[2] A. Lipp, *Ann.*, 211, 345 (1882); *Ber.*, 14, 1746 (1881).

[3] E. S. Schipper and A. R. Day, *Heterocyclic Compounds*, Vol. 5, R. C. Elderfield, ed., J. Wiley and Sons, Inc., New York, N. Y., 1957, pp. 221–2.

[4] J. W. Clark and A. L. Wilson (to Carbide and Carbon Chemicals Corporation), U. S. Patent 2,319,848 (1943).

TABLE I

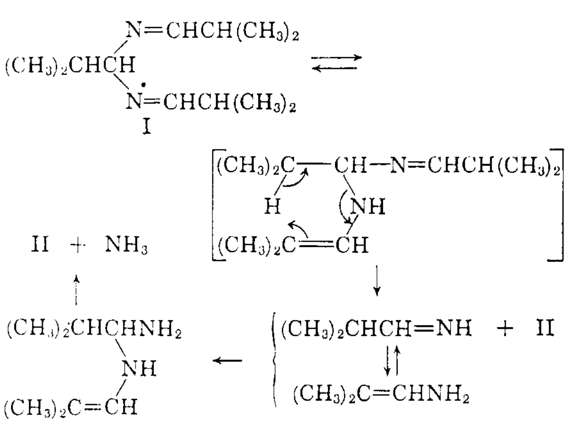
N,*N*′-DIALKYLIDENE-1,1-ALKANEDIAMINES (V)


$R-\overset{CH_3}{\underset{R'}{C}}-CH\left[N=CH\overset{CH_3}{\underset{R'}{C}}-R\right]_2$

	R	R′	B.P.	Press., Mm.	Yield, %	C		H		N	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
Va	$-CH_3$	$-CH_2CH=CH_2$	95–102	0.07–0.5	76	79.6	79.3	11.4	11.6	8.85	8.74
Vb	$-CH_3$	$-CH_2CH_2CH_3$	106–112	0.6–0.8	62	78.3	78.7	13.0	13.0	8.64	8.73
Vc	$-CH_3$	$-CH_2CH_2CN$	217–225	1.5	68	71.0	71.0	9.29	9.41	19.7	19.6
Vd	$-CH_2CH_2CH_2CH_2CH_2-$		160–162	0.4	85	80.4	79.9	11.8	11.5	7.81	7.78

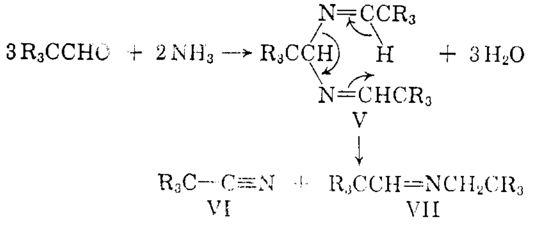
(a) and the doublet structure at (b) appeared to result from spin-spin interactions of adjacent single protons.

During slow distillation at atmospheric pressure, the hydroamide I decomposed with evolution of ammonia to form the aldimine II. The decomposition took a specific course, since II was isolated in 95% yield. This reaction might be pictured as the thermal cleavage of a tautomeric enamine form of I, with recombination of the enamine or aldimine eliminated in the primary decomposition.



The structure II was confirmed by elemental analysis and hydrogenation to diisobutylamine. The infrared spectrum of II showed strong absorptions at 6.0 μ, characteristic of C=C bonding, and at 6.15 μ, characteristic of C=N bonding.

The extension of these studies to tertiary aldehydes, R_3CCHO, showed that these aldehydes also reacted with ammonia to form "trialkylidenediamines" (V). In effect, these derivatives were aliphatic hydroamides more akin to the aromatic analog, for they contained no hydrogen atoms on the carbon next to the original carbonyl group. Disproportionation to *N*-alkylidenealkenylamines (analogous to II) was structurally impossible. However, the pyrolysis did not follow the path of the aromatic hydroamides either, but went instead through an internal oxidation-reduction reaction to the formation of a nitrile and an amine. The over-all result was superficially similar to the formation of an acid and an alcohol in a Cannizzaro reaction.[5] Of the three molecules of tertiary aldehyde involved in the formation of the hydroamide V, one molecule of aldehyde was converted to a nitrile and a second to an amine. The amine was combined into an aldimine with the third molecule of aldehyde which was otherwise unchanged. The mechanism of decomposition of V can be formulated as a conventional concerted elimination reaction.



The reaction of tertiary aldehydes with ammonia to form the hydroamides V was carried out by treatment of the aldehydes with anhydrous ammonia in the presence of potassium carbonate. The reaction mixtures apparently were equilibrium systems; conversions to V ranged from 62 to 85%, but the amounts of unchanged aldehydes indicated that corrected yields were appreciably higher. The initial condensations were conducted at room temperature or below, and the hydroamides V were isolated by distillation under reduced pressure. Analytical data for the derivatives of 2,2-dimethyl-4-pentenal (Va), 2,2-dimethylvaleraldehyde (Vb), 4-cyano-2,2-dimethylbutyraldehyde (Vc), and 1-methylcyclohexanecarboxaldehyde (Vd) are listed in Table I. These data, together with infrared absorption spectra of V and identification of the pyrolysis products, confirmed the structures of V. As an example, the infrared spectrum of Va showed principal absorption maxima at 6.0 μ and 6.1 μ and doublets at 7.2–7.35 μ and 10.05–11.0 μ, charac-

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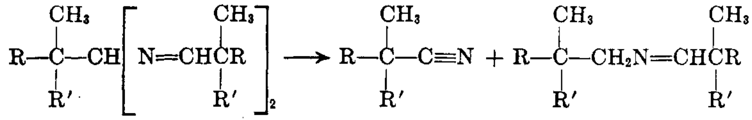
[5] A nitrogen analog of the Cannizzaro reaction was noted when benzylidenimine, heated with ammonia and potassium amide, was converted in part to benzylamine and potassium benzamidine. The major reaction product, however, was the triphenylbenzimidazole. The formation of amarine (triphenyldihydrobenzimidazole) from hydrobenzamide can be interpreted as a nitrogen analog of a successive benzoin condensation and a Cannizzaro reaction. [H. H. Strain, *J. Am. Chem. Soc.*, 49, 1563 (1927)].

TABLE II

PYROLYSES OF N,N'-DIALKYLIDENE-1,1-ALKANEDIAMINES



$$\left[R\text{—}\overset{CH_3}{\underset{R'}{C}}\text{—}CH\right]\left[N\text{=}CH\overset{CH_3}{\underset{R'}{C}}R\right]_2 \longrightarrow R\text{—}\overset{CH_3}{\underset{R'}{C}}\text{—}C\equiv N + R\text{—}\overset{CH_3}{\underset{R'}{C}}\text{—}CH_2N\text{=}CH\overset{CH_3}{\underset{R'}{C}}R$$

V VI VII

	R	R′
a.	$—CH_3$	$—CH_2CH=CH_2$
b.	$—CH_3$	$—CH_2CH_2CH_3$
c.	$—CH_3$	$—CH_2CH_2CN$
d.	$—CH_2CH_2CH_2CH_2CH_2—$	

Pyrolysis Product	Yield, %[d]	B.P.[e]	n_D^{20}	C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
VIa	79.1	147–148.5	1.4180	77.0	77.2	10.1	10.4	12.8	12.6
VIIa	81.4	218–221	1.4509	81.1	80.8	12.1	12.2	6.76	6.70
VIb	67.5	148–149.5	1.4041	75.6	76.1	11.7	12.0	12.6	12.3
VIIb	73.0	220–223	1.4365	79.6	79.9	13.7	13.5	6.64	6.53
VIc[a]	51.5	127–129[f]	1.4352	68.9	69.3	8.20	8.65	22.9	22.4
VIIc[b,c]	77.0	201–205[g]	1.4660	72.1	71.4	9.86	9.96	18.0	18.2
VId	72.8	181–182	—	78.0	77.8	10.6	10.9	11.4	10.9
VIId	76.2	259–267	—	81.6	81.5	12.4	12.3	5.95	5.89

[a] Hydrolyzed with 10% sodium hydroxide solution, then acidified to give 2,2-dimethylglutaric acid, m.p. 82–83°.[6] [b] Refluxed with excess 20% sodium hydroxide solution, acidified, and treated with 2,4-dinitrophenylhydrazine reagent to give the 2,4-dinitrophenylhydrazone of 2,2-dimethylglutaraldehydic acid, m.p. 153°.[7] [c] Acidic hydrolysis gave 4-cyano-2,2-dimethylbutyraldehyde[8] and 5-amino-4,4-dimethylvaleronitrile. The aminonitrile was saponified with 20% sodium hydroxide solution and isolated as 5,5-dimethyl-2-piperidinone, m.p. 126–127°, identical with an authentic sample prepared by reductive amination of 2,2-dimethylglutaraldehydic acid. [d] Based on V. [e] Atmospheric pressure (about 730 mm.) unless otherwise noted. [f] 9 mm. [g] 8 mm.

teristic of C=C, C=N, $C(CH_3)_2$, and nonconjugated CH_2=CH, respectively.

Pyrolysis of V was accomplished by slow distillation at atmospheric pressure. Under these conditions, thermal decomposition took place at 200–250°. Fractionation of the distillates gave the nitriles (VI) in 50–80% yields and the *N*-alkylidenealkylamines (VII) in 70–80% yields. Analytical data for these pyrolysis products are listed in Table II. The infrared spectra of the aldimines VIIa and VIIc were almost indistinguishable from those of the hydroamides Va and Vc; major peaks were the same and only minor changes in intensities were noted. The NMR spectrum of VIIc showed peaks at −90, 64, 100, 120, and in the region of 150 c.p.s. Areas under these peaks were in the ratio 1:2:4:4:12 corresponding to protons associated with CH=N, CH_2N=C, CH_2, CH_2, and CH_3, respectively. The fine structure around 150 c.p.s. indicated the presence of two types of methyl groups, with a pair of each type. The peak at 64 c.p.s. was assigned to CH_2N=C by comparison with the NMR spectrum of the aldimine of ethylamine and 4-cyano-2,2-dimethylbutyraldehyde, in which the corresponding peak was found at 65 c.p.s.

Identification was confirmed in some cases by hydrolysis of the aldimines VII to the constituent amines and aldehydes. A solution of VIIa in dilute hydrochloric acid gradually formed a water-insoluble layer, identified as the starting tertiary aldehyde. Neutralization of the acidic aqueous layer gave 2,2-dimethyl-4-pentenylamine in 74% yield. VIIc was hydrolyzed similarly to 4-cyano-2,2-dimethylbutyraldehyde and 5-amino-4,4-dimethylvaleronitrile. The structures of the nitriles VI were also checked by alkaline hydrolysis to the corresponding acids.

EXPERIMENTAL

N,N′-Diisobutylidene-2-methyl-1,1-propanediamine (I). Four hundred grams (5.6 moles) of freshly distilled isobutyraldehyde was added over a period of 1.5 hr. to a solution of 370 g. (5.9 moles) of 28% aqueous ammonia solution diluted with 210 g. of water. The reaction temperature was held at 15–25° by means of an ice bath. The mixture was stirred at room temperature for an additional 1.5 hr., and the organic layer was separated, washed with 500 ml. of water, and dried over solid potassium hydroxide. Distillation of the product through a 10-inch packed column under reduced pressure was difficult at first, due to some decomposition with evolution of ammonia. After this initial decomposition ceased, the product was distilled rapidly to give 258 g. (71%) of *N,N′*-diisobutylidene-2-methyl-1,1-propanediamine, b.p. 89–91° (14 mm.), n_D^{20} 1.4391. The base temperature of the still was not allowed to exceed 110°.

Anal. Calcd. for $C_{12}H_{24}N_2$: C, 73.4; H, 12.2; N, 14.3; mol. wt., 196. Found: C, 73.2; H, 12.3; N, 14.1; mol. wt. (cryoscopic in benzene), 184.

Pyrolysis of N,N′-diisobutylidene-2-methyl-1,1-propanediamine (I) *to N-isobutylidene-2-methylpropenylamine* (II). Seventy grams (0.35 mole) of *N,N′*-diisobutylidene-2-methyl-1,1-propanediamine was distilled slowly through a 6-inch Vigreux column at atmospheric pressure. Ammonia

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(6) W. Franke and J. Bueren, *Z. Naturforsch.*, **5b**, 122 (1950).

(7) R. H. Wiley and P. Veeravagu, *J. Org. Chem.*, **23**, 297 (1958).

(8) G. Tschudi and S. Schinz, *Helv. Chim. Acta*, **33**, 1870 (1950).

was evolved during the early stages of the distillation. After a small fraction (2.5 g.) of low-boiling material was collected, 63.3 g. (95%) of *N*-isobutylidene-2-methylpropenylamine was received, b.p. 143–144°, n_{D}^{20} 1.4603. Infrared absorption maxima (μ): 3.4, 3.45, 3.5, 3.55, 6.0, 6.15, 6.8, 7.25, 7.4, 7.5, 7.75, 8.7, 9.6, 10.35, 10.7, 10.9, 11.9.

Anal. Calcd. for $C_8H_{15}N$: C, 76.7; H, 12.0; N, 11.2. Found: C, 76.5, H, 11.9; N, 11.0.

A 60-g. sample of II was hydrogenated over 5 g. of Raney nickel (alcoholic slurry) in a stainless steel rocking-type autoclave at 120° and 3000 p.s.i. for 3 hr. After removal of the catalyst, distillation gave 52 g. (84%) of diisobutylamine, b.p. 137–138°, n_{D}^{20} 1.4090.

Anal. Calcd. for $C_8H_{19}N$: Neut. equiv., 129. Found: 129.

Reaction of this product with phenyl isothiocyanate gave the phenylthiourea derivative of diisobutylamine, m.p. 120–121°.[9]

Condensation of ammonia and tertiary aldehydes. 2,2-Dimethyl-4-pentenal was prepared by the acid-catalyzed reaction of allyl alcohol and isobutyraldehyde, and 2,2-dimethylvaleraldehyde was obtained by hydrogenation of this product.[10] 4-Cyano-2,2-dimethylbutyraldehyde was prepared by the condensation of acrylonitrile and isobutyraldehyde with potassium cyanide [11,12] or an ion-exchange [13] catalyst. 1-Methylcyclohexanecarboxaldehyde was prepared by palladium-catalyzed hydrogenation of 1-methyl-3-cyclohexene-1-carboxaldehyde, obtained by condensation of butadiene and methacrolein.[14]

Experimental details are noted only for the synthesis of the hydroamide Va from 2,2-dimethyl-4-pentenal and its pyrolysis to the nitrile VIa and aldimine VIIa. Reactions with other derivatives (Tables I and II) were conducted in an analogous manner.

(a) *2,2-Dimethyl-N,N'-bis(2,2-dimethyl-4-pentenylidene)-4-pentene-1,1-diamine* (Va). A suspension of 10 g. of anhydrous potassium carbonate in 250 g. (2.2 moles) of 2,2-dimethyl-4-pentenal was placed in an ice bath and saturated with ammonia. Absorption practically ceased after absorption of 37.4 g. (2.2 moles) of ammonia. The flask was stoppered loosely and left at room temperature for 2 days; at the end of this time, 30 g. (1.8 moles) of ammonia was left in solution. The lower aqueous layer was removed, and the organic layer was distilled through an 8-inch × 1-inch diameter column packed with stainless steel protruded packing. After removal of 41 g. of low-boiling material, 177 g. (76%) of 2,2-dimethyl-*N,N'*-bis(2,2-dimethyl-4-pentenylidene)-4-pentene-1,1-diamine (Va) was received, boiling from 102° (0.5 mm.) to 95° (0.07 mm.), n_{D}^{20} 1.4670, d_4^{20} 0.8478. The distillation residue amounted to 12.7 g.

Redistillation of the forerun through this same column at atmospheric pressure gave 2 g., b.p. 118–123°, n_{D}^{20} 1.4190, and 13 g., b.p. 123–125°, n_{D}^{20} 1.4199, of unreacted 2,2-dimethyl-4-pentenal.

(b) *Pyrolysis of 2,2-dimethyl-N,N'-bis(2,2-dimethyl-4-pentenylidene)-4-pentene-1,1-diamine* (Va). A 150-g. sample of Va was distilled slowly at atmospheric pressure through the distillation column used previously. The initial base temperature was 245° and the head temperature, 149°. During the 3 hr. required for the distillation, the base and head temperatures rose gradually to 360° and 215° maximum. The distillate weighed 142 g.; the residue, 6.5 g. The distillate was redistilled carefully through the column at atmospheric pressure to give a 2.5-g. forerun, b.p. 145–147°, n_{D}^{20} 1.4188; 41 g. of 2,2-dimethyl-4-pentenenitrile (VIa), b.p. 147–148.5°, n_{D}^{20} 1.4180, d_4^{20} 0.8101; an intermediate fraction of 12.7 g., b.p. 148.5–218°, and 80 g. of *N*-(2,2-dimethyl-4-pentenylidene)-2,2-dimethyl-4-pentenylamine (VIIa), b.p. 218–221°, n_{D}^{20} 1.4509, d_4^{20} 0.8087.

VIa was characterized by saponification with aqueous sodium hydroxide solution, followed by acidification to give a crude acid. The *p*-bromophenacyl ester, m.p. 59–61.5°, was checked in admixture with the corresponding ester of authentic 2,2-dimethyl-4-pentenoic acid, m.p. 61.5–63°. The melting point was not depressed.

Anal. Calcd. for $C_{15}H_{17}BrO_3$: C, 55.4; H, 5.23; Br, 24.6. Found: C, 55.2; H, 5.27; Br, 24.6.

A 76.5-g. sample of VIIa was stirred at room temperature with a solution of 50 g. of concd. hydrochloric acid in 50 ml. of water. The mixture warmed spontaneously and became clear, then clouded gradually. After the mixture had been stirred at room temperature for 2 hr., the organic layer was separated and the aqueous layer was extracted with ether until residual aldehyde gave only a faint test with 2,4-dinitrophenylhydrazine reagent. The combined organic layer and ether extracts were dried over sodium sulfate and distilled to give, after removal of ether, 29 g. of 2,2-dimethyl-4-pentenal, b.p. 120–125°, n_{D}^{20} 1.4198.

Anal. Calcd. for $C_7H_{12}O$: C, 74.9; H, 10.7. Found: C, 74.4; H, 10.7.

The aqueous layer from the ether extractions was made strongly alkaline with solid potassium hydroxide. The organic layer was separated, and the aqueous layer was extracted several times with ether. The combined organic layer and extracts were dried over potassium hydroxide pellets and distilled. After removal of a forerun, 31 g. of 2,2-dimethyl-4-pentenylamine was removed, b.p. 130–133.5°, n_{D}^{20} 1.4378.

Anal. Calcd. for $C_7H_{15}N$: C, 74.3; H, 13.3; N, 12.4; neut. equiv., 113. Found: C, 74.1; H, 13.4; N, 12.1; neut. equiv., 113.

The amine gave a phenylthiourea derivative melting at 81.5–83.0°.

Acknowledgment. We are indebted to C. A. Boye, J. H. Chaudet, and Charlotte P. Hill, of these laboratories, for the determination and interpretation of infrared and NMR spectra, and to R. G. Nations for the preparation of 1-methylcyclohexanecarboxaldehyde and its ammonia derivatives.

KINGSPORT, TENN.

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(9) Various literature sources (see R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., J. Wiley and Sons, Inc., New York, N. Y., 1956, p. 234) report a melting point of 113° for 1,1-diisobutyl-3-phenyl-2-thiourea. Our preparation of this derivative from authentic diisobutylamine (Eastman Organic Chemicals, No. 4035) had a melting point of 120–121°.

(10) K. C. Brannock, *J. Am. Chem. Soc.*, **81,** 3379 (1959).

(11) W. E. Thiele and W. Franke, *Office of Technical Services Report No.* **PB 35,103,** U. S. Dept. of Commerce (1944).

(12) D. Hoch and P. Karrer, *Helv. Chim. Acta*, **37,** 397 (1954).

(13) E. D. Bergmann and R. Corett, *J. Org. Chem.*, **23,** 1507 (1958).

(14) H. Pines, F. J. Paulik, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **73,** 5740 (1951).