

Anal.:¹⁰ Calcd. for $C_{13}H_8N_4$: C, 70.89; H, 3.66. Found: C, 70.65; H, 3.77.

B. From fluorenone oxime. To a mixture of 10 g. (0.05 mole) of fluorenone oxime and 15 g. (0.07 mole) of phosphorus pentachloride was cautiously added 100 ml. of phosphorus oxychloride; a vigorous reaction began at once. After two hours of refluxing, the mixture had turned black. The phosphorus oxychloride was removed by distillation after the addition of 25 ml. of xylene as diluent and chaser, and a solution of ca. 0.1 mole of hydrogen azide in 200 ml. of dry benzene was added to the cold residue. After one week at room temperature, the solution was heated for 0.5 hr., cooled and washed thoroughly with 20% sodium carbonate solution. The dried (magnesium sulfate) and filtered solution was concentrated to near dryness, heated with absolute alcohol, filtered from some insoluble matter, and crystallized by the addition of water to give 2.06 g. (18.4%), m.p. 208–218°. A sample recrystallized from aqueous ethanol gave no depression of melting point when mixed with the compound obtained from 2-azido-2'-cyanobiphenyl.

Pyrolysis of 4-Azidofluorenone. When 1.0 g. samples of 4-azidofluorenone were heated in kerosine or resorcinol dimethyl ether solution, nitrogen was evolved at about 175° and the solutions turned nearly black. On cooling, a brown, amorphous solid separated, insoluble in benzene or ethanol, but soluble in nitrobenzene. Attempts at crystallization, with and without chromatography, failed, as did attempts to prepare a picrate and an oxime.

4-Aminofluorene. A mixture of 5.00 g. (0.0238 mole) of fluorene-4-carboxylic acid¹¹ and 5.95 g. (0.05 mole) of thionyl chloride was heated on a steam bath for one hour and the

excess thionyl chloride was distilled off. A solution of 3.25 g. (0.05 mole) of sodium azide in 15 ml. of water was added with stirring to a solution of the resulting acid chloride in 25 ml. of acetone. The light orange-brown, crude, solid azide was collected after the addition of 50 ml. of water, and was pressed dry and promptly dissolved in 60 ml. of benzene. After 0.5 hr. of refluxing, nitrogen evolution had stopped, and 25 ml. of 50% potassium hydroxide solution was added and the refluxing continued for several hours. Hydrogen chloride was passed into the separated and dried benzene layer, precipitating 3.28 g. (63.5%) of 4-aminofluorene hydrochloride, m.p. 240° (dec.). A purer sample was prepared by releasing the free base with aqueous ammonia, taking it up in benzene, and reprecipitating with hydrogen chloride, which gave a white solid, m.p. 283–288°.

Anal.:¹⁴ Calcd. for $C_{13}H_{12}NCl$: C, 71.69; H, 5.56. Found: C, 71.82; H, 5.70.

The free base was obtained by decomposing the salt with aqueous ammonia and crystallizing from benzene. It formed pale yellow needles, m.p. 112.5–114°.

Anal.:¹⁴ Calcd. for $C_{13}H_{11}N$: C, 86.16; H, 6.12. Found: C, 86.02; H, 6.09.

Pyrolysis of 4-azidofluorene. Attempted thermal cyclization of 4-azidofluorene in the same manner as described for 4-azidofluorenone gave an amorphous, brown solid of similar characteristics, that resisted all attempts at crystallization.

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(31) W. E. Bachmann and J. C. Sheehan, *J. Am. Chem. Soc.*, **62**, 2689 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Synthesis of Some 1,1-Dibenzylhydrazines¹

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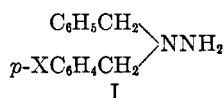
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A series of unsymmetrically substituted dibenzylhydrazines, $p\text{-XC}_6\text{H}_4\text{CH}_2\text{NCH}_2\text{C}_6\text{H}_5$, where X = $\text{CH}_3\text{O}-$, $(\text{CH}_3)_2\text{N}-$,



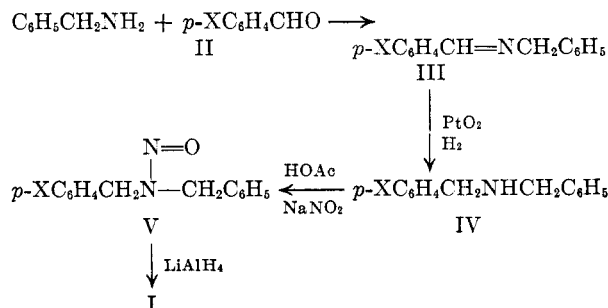
CH_3- , and $\text{Cl}-$, have been prepared by reduction of the corresponding nitrosamines with lithium aluminum hydride. 1-Benzyl-1-furfurylhydrazine was also prepared by this method. Attempts to prepare other hydrazines of this type are discussed.

In connection with a current investigation of the oxidation of 1,1-dibenzylhydrazines, it was necessary to prepare a number of disubstituted hydrazines of the general formula I.



The hydrazines were all prepared by the same general route. Benzylamine and a suitably substituted benzaldehyde (II) were condensed to give a Schiff base (III). III was reduced in absolute ethanol in the presence of platinum oxide to a secondary amine (IV) which was then nitrosated in

dilute acetic acid solution to give a nitrosamine (V). The latter was reduced with lithium aluminum hydride to the corresponding 1,1-dibenzylhydrazine (I). The properties of the products are listed in Tables I–V.



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TABLE I
 SCHIFF BASES: RCH = NCH₂C₆H₅^a(III)

R	Yield, %	M.P., or B.P. Mm.	Lit. M.P., or B.P. Mm.
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄ ^b	63	76-77 ^c	
<i>p</i> -CH ₃ SO ₂ C ₆ H ₄ ^b	66	72.5-74 ^d	
<i>p</i> -CH ₃ OC ₆ H ₄	77	39-40	42 ^e
<i>p</i> -CH ₃ C ₆ H ₄	76	207(24)	210(25) ^f
<i>p</i> -ClC ₆ H ₄	81	34-36	34 ^f
<i>p</i> -NO ₂ C ₆ H ₄	70	55-57 ^g	56 ^g
2-furyl	60	158-159(12)	155(11) ^h
<i>p</i> -OHC ₆ H ₄	93	202-204 ⁱ	205-206 ⁱ

^a Prepared by heating benzylamine and the appropriate aldehyde in the absence of a solvent except where noted otherwise. ^b Recrystallized from ether. ^c Calcd. for C₁₆H₁₅N₂: C, 80.62; H, 7.63; N, 11.76. Found: C, 80.33; H, 7.58; N, 11.37. ^d Calcd. for C₁₅H₁₅NO₂S: C, 65.90; H, 5.54; N, 5.13. Found: C, 65.63; H, 5.46; N, 5.47. ^e Ref. 7. ^f C. Shoppee, *J. Chem. Soc.*, 1225 (1931). ^g This product was obtained only when an ethereal solution was allowed to stand for several hours [C. K. Ingold and H. Piggott, *J. Chem. Soc.*, 121, 2381 (1922)]. The procedure of footnote *a* invariably yielded a light yellow solid, m.p. 193-195°, of unknown structure. ^h G. De Chamot, *Ann.*, 271, 11 (1892). ⁱ A. Mason and G. Winder, *J. Chem. Soc.*, 65, 192 (1894). ^j This value seems unusually high compared to the melting points of the other Schiff bases. The same compound was obtained using the method described in footnote *g*. The structure of the product is supported by its ultraviolet absorption spectrum (λ_{\max} 273 m μ , log a_M 4.25) which shows a reasonable relationship to that reported for *N*-(*p*-methoxybenzylidene)benzylamine (λ_{\max} 268 m μ , log a_M 4.30) [P. Grammaticakis, *Bull. soc. chim.*, (5), 427 (1941)].

also was attempted with sodium borohydride in the presence of aluminum chloride. In this case the reduction failed and 74% of the starting material was recovered. The reduction was then attempted employing lithium aluminum hydride in the manner suggested by Felkin⁴ who had successfully reduced ester groups without affecting aromatic nitro groups. This method also failed and the starting material was again recovered along with a small amount of orange solid which was not the desired hydrazine.

The hydrazines were all colorless or light yellow liquids which appeared to suffer oxidation and deterioration upon exposure to the atmosphere. The hydrazines were identified as the hydrazones of *p*-nitrobenzaldehyde (Table V). In several cases the hydrochlorides of the hydrazines were prepared; however, difficulties were encountered in purification and their physical properties are not reported here.

From the lithium aluminum hydride reduction of *N*-nitroso-*N*-(*p*-methanesulfonylbenzyl)benzylamine, a compound thought to be 1-benzyl-1-(*p*-methanesulfonylbenzyl)hydrazine was obtained. It could not be purified by distillation. The crude product reacted with oxalic acid, forming what appeared to be an oxalate salt, but analysis of this salt did not agree with values calculated for an oxalate of 1-benzyl-1-(*p*-methanesulfonylbenzyl)-

 TABLE II
 SECONDARY AMINES: RCH₂NHCH₂C₆H₅ (IV)

R	Time Required for Reduction of Schiff Base, Hr. ^a	Yield, %	M.P. or B.P. (Mm.)	Lit. M.P. or B.P. (Mm.)
<i>p</i> -CH ₃ OC ₆ H ₄ ^b	2	92	193-194 (7)	206(10) ^c
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄ ^d	1	82	190-194(1-2)	
<i>p</i> -CH ₃ SO ₂ C ₆ H ₄ ^e	18	69	...	
<i>p</i> -CH ₃ C ₆ H ₄ ^f	1	92	147(2)	
<i>p</i> -ClC ₆ H ₄	2	67	192(10)	193-196(13) ^g
<i>p</i> -NO ₂ C ₆ H ₄	..	49	247-249 ^h	
2-furyl	6	77	127-134(5)	115-124(4) ⁱ
<i>p</i> -OHC ₆ H ₄	1	^j		

^a All reductions were carried out in absolute ethanol according to the directions in *Org. Reactions*, IV, p. 197 (1948), with the exception of *N*-(*p*-methanesulfonylbenzylidene)benzylamine which was reduced in absolute methanol and *N*-(*p*-hydroxybenzylidene)benzylamine which was reduced in dimethylformamide. ^b n_D^{25} 1.5728, d_4^{25} 1.078. ^c Ref. 8. ^d n_D^{25} 1.5984, d_4^{25} 1.035. ^e This material was not purified. Derivative: 1-benzyl-1-(*p*-methanesulfonylbenzyl)-3-phenyl-2-thiourea. Calcd. for C₂₂H₂₂N₂S₂O₃: C, 64.35; H, 5.29; N, 6.82. Found: C, 64.06; H, 5.39; N, 7.14. ^f n_D^{25} 1.5660; d_4^{25} 1.018. Derivative: 1-benzyl-1-(*p*-methylbenzyl)-3-phenyl-2-thiourea. Calcd. for C₂₂H₂₂N₂S: C, 76.25; H, 6.41. Found: C, 76.42; H, 6.33. ^g J. V. Braun, M. Kuhn, and J. Weismantel, *Ann.*, 449, 249 (1926). ^h Melting point of hydrochloride, in which form the amine was isolated. ⁱ K. N. Campbell, J. F. Ackerman, B. K. Campbell, *J. Am. Chem. Soc.*, 71, 2905 (1949). ^j Although the reaction mixture rapidly took up the calculated quantity of hydrogen, the product decomposed during distillation. No product could be isolated from attempts to nitrosate the crude product from the hydrogenation.

The preparation of *N*-(*p*-nitrobenzyl)benzylamine differed from the general procedure in the use of sodium borohydride and aluminum chloride³ to reduce the carbon-nitrogen double bond of the Schiff base without affecting the nitro group. The reduction of *N*-nitroso-*N*-(*p*-nitrobenzyl)benzylamine

hydrazine. Attempts to prepare a hydrazone with *p*-nitrobenzaldehyde and to prepare the 4-phenyl-3-thiosemicarbazide with phenyl isothiocyanate were unsuccessful. For these reasons the identity of the reduction product remains in doubt.

(3) H. C. Brown and B. Subba Rao, *J. Am. Chem. Soc.*, 78, 2582 (1956).

(4) H. Felkin, *Compt. rend.*, 230, 304 (1950).

TABLE III
Nitrosamines: $RCH_2NCH_2C_6H_5$ (V)
|
N = O

R ^a	Yield, %	M.P., B.P., °C., (Mm.)	Formula	Calcd.			Found		
				C	H	N	C	H	N
<i>p</i> -CH ₃ OC ₆ H ₄	91	53-55	C ₁₅ H ₁₆ N ₂ O ₂	74.34	7.50	...	74.07	7.18	...
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	55	60-63	C ₁₆ H ₁₉ N ₃ O	71.33	7.12	15.60	71.13	7.24	15.73
<i>p</i> -CH ₃ SO ₂ C ₆ H ₄	64	86-88	C ₁₅ H ₁₆ N ₂ O ₃ S	59.18	5.31	9.21	58.62	5.19	9.24
<i>p</i> -CH ₃ C ₆ H ₄ ^b	87	176-177(3)	C ₁₅ H ₁₆ N ₂ O	74.96	6.72	11.66	75.09	6.59	11.57
<i>p</i> -ClC ₆ H ₄	74	190(2)	C ₁₄ H ₁₃ N ₂ OCl	64.48	5.04	...	64.19	4.70	...
α -Furyl ^c	67	158-164(4)	C ₁₂ H ₁₂ N ₂ O ₂	66.64	5.60	12.96	66.40	5.23	12.80
<i>p</i> -NO ₂ C ₆ H ₄	95	78-80	C ₁₄ H ₁₃ N ₂ O ₃	61.97	4.84	15.49	62.98	4.55	14.39

^a All the nitrosamines were recrystallized from 95% ethanol with the exception of *N*-nitroso-*N*-(*p*-methoxybenzyl)benzylamine, which was recrystallized from absolute ethanol. ^b n_D^{25} 1.5783, d_4^{25} 1.145. ^c n_D^{27} 1.5582, d_4^{27} 1.158.

TABLE IV

1,1-Dibenzylhydrazines: $RCH_2NCH_2C_6H_5$ (I) ^a				
R	Yield, %	B.P. (Mm.)	n_D'	d_4'
<i>p</i> -CH ₃ OC ₆ H ₄	67	185-188 (0.5-1)	1.5815 ¹⁸	1.067 ²⁵
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	50	188-190 (1)	1.5983 ¹⁸	1.073 ²⁸
<i>p</i> -CH ₃ C ₆ H ₄	71	144-146 (1)	1.5737 ²⁶	1.064 ^{24,5}
<i>p</i> -ClC ₆ H ₄	71	165-167 (1)	1.5855 ²⁷	1.132 ²³
α -Furyl	58	132-134 (3)	1.552 ³⁰	1.087 ³¹

^a Reduction of corresponding nitrosamine carried out by method of Schueler and Hanna [*J. Am. Chem. Soc.*, **74**, 3693 (1952)]. The rate of addition of the nitrosamine solution was not permitted to exceed one drop per second to keep the reaction from taking place with explosive violence [L. F. Audrieth, *et al.*, *J. Am. Chem. Soc.*, **77**, 790 (1955)].

solution had been added, the mixture was stirred at room temperature for 30 min. and then heated on a steam bath for 1.5 hr. The reaction mixture was then cooled and poured into 70 g. of crushed ice and 12 ml. of concentrated hydrochloric acid. A light yellow precipitate was removed by filtration and recrystallized from 200 ml. of 95% ethanol. A white precipitate was obtained which weighed 9.5 g. (49%) and melted at 247-249°. This precipitate gave a positive Beilstein test for halogen and a Hinsberg test for a secondary amine.

Anal. Calcd. for C₁₄H₁₅ClN₂O: C, 60.31; H, 5.44. Found: C, 60.97; H, 5.52.

Attempt to reduce N-nitroso-N-(p-nitrobenzyl)benzylamine with sodium borohydride. The procedure was the same as that employed in the preparation of *N*-(*p*-nitrobenzyl)benzylamine hydrochloride. From 3.5 g. (0.01 mole) of *N*-nitroso-*N*-(*p*-nitrobenzyl)benzylamine, 0.4 g. (0.01 mole) of sodium borohydride, and 0.5 g. (0.004 mole) of aluminum chloride, an oil was obtained which solidified upon cooling. The solid was recrystallized from 95% ethanol to yield 2.6 g. of a light yellow solid, m.p. 76-80°. A mixed m.p. of 76-80° was obtained with a sample of *N*-nitroso-*N*-(*p*-nitrobenzyl)benzylamine (m.p. 78-80°). This represented a 74% recovery of starting material.

Attempt to reduce N-nitroso-N-(p-nitrobenzyl)benzylamine

TABLE V
Hydrazones of *p*-nitrobenzaldehyde: $R-CH_2NN=CHC_6H_4NO_2$

R ^a	M.P., °C.	Formula	Calcd.			Found		
			C	H	N	C	H	N
<i>p</i> -CH ₃ OC ₆ H ₄ ^b	76-77	C ₂₁ H ₂₂ N ₃ O ₃	70.37	5.65	11.19	70.25	5.86	11.59
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	110-111	C ₂₃ H ₂₄ N ₄ O ₂	71.13	6.24	14.43	71.00	6.09	14.52
<i>p</i> -CH ₃ C ₆ H ₄	123-125	C ₂₂ H ₂₁ N ₃ O ₂	73.50	5.90	11.69	73.41	5.43	11.49
<i>p</i> -ClC ₆ H ₄	122.5-123.5	C ₂₂ H ₁₉ N ₃ O ₂ Cl	66.39	4.79	...	66.45	4.65	...
α -Furyl-	65-66	C ₁₉ H ₁₇ N ₃ O ₃	68.04	5.12	12.53	68.40	5.28	12.54

^a The procedure employed was that of R. L. Shriner, R. C. Fuson and D. Y. Curtin, *Systematic Identification of Organic Compounds*, 4th Edition, Wiley & Sons, New York, New York, 1956, p. 219. ^b This hydrazone was recrystallized from absolute ethanol. All the others were recrystallized from 95% ethanol.

EXPERIMENTAL⁵

With the exception of the reactions described below, the hydrazines were prepared by well-known procedures.

N-(*p*-Nitrobenzyl)benzylamine hydrochloride. A solution of 1.2 g. (0.35 mole) of sodium borohydride and 16.9 g. (0.07 mole) of *N*-(*p*-nitrobenzylidene)benzylamine in 100 ml. of tetrahydrofuran was vigorously stirred as 1.6 g. (0.01 mole) of aluminum chloride in 50 ml. of tetrahydrofuran was added, at such a rate that the temperature of the reaction did not rise above 50°. After all of the aluminum chloride

with lithium aluminum hydride. The procedure employed was that of Felkin.⁴ From 7.4 g. (0.03 mole) of *N*-nitroso-*N*-(*p*-nitrobenzyl)benzylamine and 0.4 g. (0.01 mole) of lithium aluminum hydride a light orange solid, m.p. 68-76°, was obtained. After two recrystallizations of this material from 80% ethanol two products were obtained. One was a light yellow solid which melted at 80-81° and did not depress the melting point of an authentic sample of *N*-nitroso-*N*-(*p*-nitrobenzyl)benzylamine. The other product was a light orange solid which melted at approximately 135° and did not have the properties of the desired hydrazone.

(5) Melting points and boiling points are uncorrected.