solved in 100 ml of 6 *N* hydrochloric acid and allowed to stand at room temperature for 14–18 hr. The acid solution was concentrated to about 50 ml on a rotary vacuum evaporator. At this point the products precipitated and were separated by filtration and washed with cold absolute ethanol. The compounds could be recrystallized with difficulty and considerable loss from ethanol. Since recrystallization did not seem to raise the melting points and the compounds were homogeneous on tlc (1:25 ammonia–methanol on silica gel G), the crude products were judged pure and were analyzed directly.

Derivatives of 6.—The picrate of **6** was prepared from the hydrochloride and recrystallized from ethanol to yield an analytical sample, mp 185–187°.

Anal. Calcd for $C_{16}H_{16}N_4O_{10}$: C, 45.29; H, 3.80; N, 13.20. Found: C, 45.25; H, 4.01; N, 13.40.

The free base of **6** was prepared by basification, with ammonia, of a concentrated aqueous solution of the hydrochloride. It melted at 218–219° and was washed with cold ethanol prior to analysis.

Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.17. Found: C, 61.98; H, 6.99; N, 7.22.

1,2,3,4-Tetrahydroisoquinolines (5).—The 4-hydroxy-1,2,3,4-tetrahydroisoquinolines in 0.02-mole amounts were dissolved in the minimum of cold 6 *N* hydrochloric acid and an amount of 5% palladium-on-carbon equal to the weight of the compound was added. Hydrogenation was carried out at atmospheric pressure and room temperature. The catalyst was removed by filtration and the acid solutions were evaporated to small volumes. Addition of ethanol caused precipitation of the 1,2,3,4-tetrahydroisoquinoline hydrochlorides. In the case of the compounds derived from **8** and **9**, an appreciable amount of product remained with the catalyst and was removed by washing it with boiling methanol which was subsequently added to the aqueous filtrates.

6-Hydroxy-7-methoxy-1,2,3,4-tetrahydroisoquinoline (derived from **6**) was obtained in 90% yield and melted at 259–260° (lit.[3] mp 260–263°).

6,7-Methylenedioxy-1,2,3,4-tetrahydroisoquinoline was obtained in 85% yield andm elted at 276–278° (lit.[12] mp 315°). An analytical sample was recrystallized from ethanol.

Anal. Calcd for $C_{10}H_{12}NO_2Cl$: C, 56.20; H, 5.62; N, 6.56; Cl, 16.63. Found: C, 56.59; H, 5.82; N, 6.67; Cl, 17.02.

5,8-Dihydroxy-1,2,3,4-tetrahydroisoquinoline was obtained in 40% yield. The analytical sample was recrystallized from ethanol and melted at 265–267°.

Anal. Calcd for $C_9H_{12}NO_2Cl$: C, 53.60; H, 5.96; N, 6.95; Cl, 17.62. Found: C, 53.39; H, 6.08; N, 7.16; Cl, 17.89.

8-Hydroxy-7-methoxy-1,2,3,4-tetrahydroisoquinoline was obtained in 85% yield and melted at 280–282° (lit.[3] mp 280–283°).

Periodate Oxidation of 7.—Compound **7** (0.1114 g) was dissolved in 5 ml of water and combined with 5 ml of 0.3 *M* sodium metaperiodate. Aliquots of 2 ml were removed at timed intervals and analyzed by the arsenite method.[13] The results were 1 min, 1.05 *M* equiv of periodate; 5 min, 1.08; 15 min, 1.12, and 25 min, 1.20.

The formaldehyde assay[10] was carried out on compounds **6** to **9** with the following results: **6**, 66% of formaldehyde formed; **7**, 40%; **8**, 71%; and **9**, 46%. In each case the methone of formaldehyde obtained was identical with an authentic sample.

Registry No.—6 (free base), 15051-98-6; **6**, 15051-99-7; **6** picrate, 15052-00-3; **7**, 15052-01-4; **8**, 15052-02-5; **9**, 15052-03-6; 6-hydroxy-7-methoxy-1,2,3,4-tetrahydroisoquinoline, 1011-43-4; 6,7-methylenedioxy-1,2,3,4-tetrahydroisoquinoline hydrochloride, 15052-05-8; 5,8-dihydroxy-1,2,3,4-tetrahydroisoquinoline hydrochloride, 15052-06-9; 8-hydroxy-7-methoxy-1,2,3,4-tetrahydroisoquinoline, 1610-72-6.

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(12) J. S. Buck, *J. Am. Chem. Soc.*, **56**, 1769 (1934). The discrepancy between these melting points is not readily explained. The nmr spectrum of this compound was in complete agreement with the several similar materials prepared in this laboratory.[3]

(13) P. F. Fleury and J. Lange, *J. Pharm. Chim.*, [8], **17**, 107 (1933).

3-Substituted Amino-4,5-Disubstituted 1,2,4-4H-Triazole and Aldehyde from 1-Acylsemicarbazide[1]

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Symmetrical diacylhydrazines react with primary amines in the presence of anhydrous zinc chloride to afford 3,4,5-trisubstituted 1,2,4-4H-triazoles[3]. We have now found that 1-benzoylsemicarbazide (Ia) and 1-isonicotinylsemicarbazide (Ib) react with primary amines in the presence of anhydrous zinc chloride to give 3-substituted amino-4,5-disubstituted 1,2,4-4H-triazoles (II). The structure of the triazole (IIa) was confirmed by unambiguous syntheses from 1-benzoyl-4-phenylsemicarbazide (IIIa) as well as from 2-anilino-5-phenylfuradiazole[4] in the presence of aniline and anhydrous zinc chloride. The formation of the triazoles II presumably occurs by initial formation of the semicarbazide III (Scheme I).

A characteristic decomposition of I has also been observed at 260–270° in the presence of anhydrous sodium carbonate giving rise to the aldehyde V in about 15 to 18% yield along with ammonia, carbon monoxide, and nitrogen. This reaction depends on the nature of acyl group; an alkarylacylsemicarbazide (Id) fails to afford the corresponding aldehyde under similar conditions. The formation of the aldehyde evidently proceeds *via* the acyldiimide (IV), reminiscent of the McFadyen and Stevens[5] reaction, but unlike the latter, decomposition of I could not be effected in solvents like ethylene glycol or cyclohexanol. The yield of the aldehyde could not be improved by using potassium carbonate.

It has been observed that 1-acylsemicarbazide–4-substituted 1-acylsemicarbazide can be prepared in good yield by heating a mixture of acylhydrazine and urea or substituted urea in aqueous or alcoholic medium. An attempt to prepare Ib by refluxing isonicotinic acid hydrazide and ureathane was unsuccessful. However a different reaction was observed resulting in the formation of symmetrical diisonicotinylhydrazine[6] (VI) and 2-(4-pyridyl)-1,3,4-oxadiazol-5-one[7] (VII). The product, VI, has obviously been formed by the interaction of two molecules of the hydrazide with elimination of one molecule of hydrazine,[8] whereas VII appears to be formed through the cyclization of the intermediate 1-isonicotinyl-2-carbethoxyhydrazine.[7]

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(1) Presented in part at the Joint Convention of the Indian Chemical Society and Chemical Research Committee of the Council of Scientific and Industrial Research, Aligarh, India, 1965. See also S. Dutta, B. P. Das, and U. P. Basu, *Current Sci. India*, **34**, 18 (1965).

(2) To whom the correspondence is to be addressed.

(3) R. Stolle, *Ber.*, **32**, 796 (1899); R. H. Wiley and A. J. Hart, *J. Org. Chem.*, **18**, 1368 (1953).

(4) K. Moeckel and H. Gehlen, East German Patent 36,261 (1965); *Chem. Abstr.*, **63**, 4306 (1965).

(5) J. S. McFadyen and T. S. Stevens, *J. Chem. Soc.*, 584 (1936).

(6) H. H. Fox and J. T. Gibas, *J. Org. Chem.*, **17**, 1653 (1952).

(7) A. E. Smith, *Science*, **114**, 514 (1954).

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SCHEME I

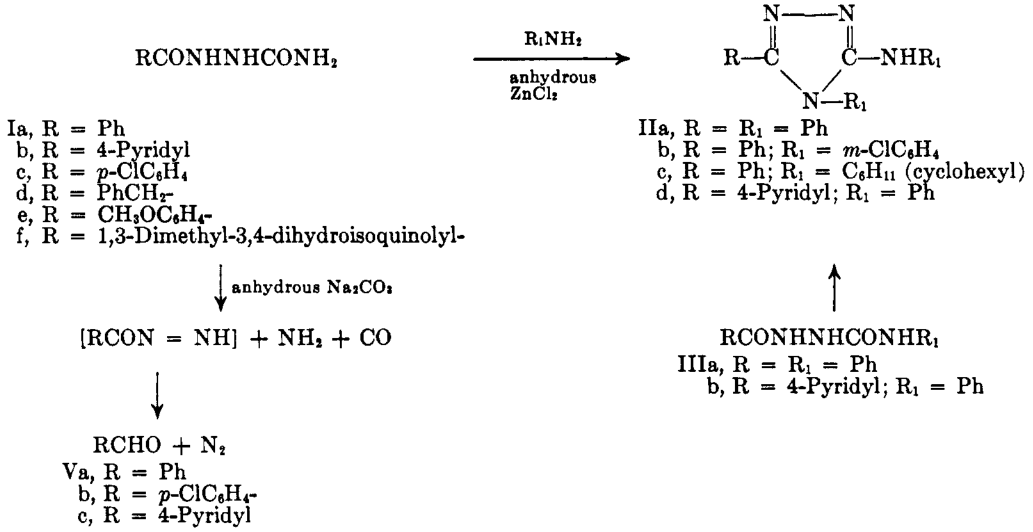

TABLE I

Acyl hydrazine used in the preparation	Compd	Yield, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Benzoylhydrazine[a]	Ia	85	226 dec	$C_8H_9N_3O_2$	53.6	5.03	23.5	53.3	5.1	23.3
p-Chlorobenzoylhydrazine[b]	Ic	83	225–226 dec	$C_8H_8N_3O_2Cl$	44.9	3.7	19.7	45.1	3.5	19.6
Phenacetylhydrazine[c]	Id	85	170–172	$C_9H_{11}N_3O_2$	55.9	5.7	21.7	55.7	5.6	21.5
p-Methoxybenzoylhydrazine[d]	Ie	85	226–227 dec	$C_9H_{11}N_3O_3$	51.6	5.3	20.1	51.7	5.1	19.8
1,3-Dimethyl-3,4-dihydroisoquinoline-3-carboxhydrazine[e]	If	86	193–194	$C_{13}H_{16}N_4O_2$	60.0	6.1	21.5	59.8	5.9	21.4

[a] T. Curtius and C. Sturve, *J. Prakt. Chem.*, [2] **50**, 295 (1894). [b] R. Kahl, *Chem. Zentr.*, **2**, 1493 (1904). [c] T. Curtius and E. Boetzelen, *J. Prakt. Chem.*, [2] **64**, 314 (1901). [d] P. P. T. Sah and K. S. Chang, *Ber.*, **69**, 2769 (1936). [e] T. N. Ghosh and Bhabatosh Bhattacharya, *J. Indian Chem. Soc.*, **36**, 425 (1959).

Experimental Section[9]

1-Isonicotinylsemicarbazide (Ib).—A mixture of isonicotinic acid hydrazide (13.6 g, 0.1 mole), urea (16.6 g, 0.28 mole), and water (40 ml) was refluxed for 8 hr during which evolution of ammonia was observed. The solid that separated on cooling was dissolved in sodium hydroxide solution (10%), treated with charcoal, filtered, and acidified with hydrochloric acid (10%) at pH 6. The white crystalline solid that separated was purified by crystallization from water to afford Ib in colorless shining needles (17 g), mp 244° dec (lit.[10] mp 243° dec).

Anal. Calcd for $C_7H_8N_4O_2$: C, 46.5; H, 4.4; N, 31.2. Found: C, 46.7; H, 4.4; N, 31.1.

The product is soluble in both acid and alkali and reduces iodine solution in presence of sodium bicarbonate.

1-Acylsemicarbazides (I) prepared as above are given in Table I.

1-Benzoyl-4-phenylsemicarbazide (IIIa).—A mixture of benzoylhydrazine (6 g, 0.044 mole), phenylurea (6 g, 0.05 mole), and water (15 ml) was heated for 6 hr at 135–140° (oil bath temperature). The solid that separated on cooling was crystallized from water to furnish IIIa (6 g) as white needles, mp 212–214°.

Anal. Calcd for $C_{14}H_{13}N_3O_2$: N, 16.5. Found: N, 16.4.

It is soluble in dilute alkali and reduces iodine solution in presence of sodium bicarbonate.

1-Isonicotinyl-4-phenylsemicarbazide (IIIb) was prepared exactly as above in white needles, mp 219–220°.

Anal. Calcd for $C_{13}H_{12}N_4O_2$: N, 21.9. Found: N, 21.6.

4,5-Diphenyl-3-anilino-1,2,4-4H-triazole (IIa). A.—A mixture of 1-benzoylsemicarbazide (6 g, 0.033 mole), freshly distilled aniline (6.2 g, 0.067 mole), and fused zinc chloride (10 g, 0.07 mole) protected from moisture was heated at 180–190° for 6 hr. The odor of ammonia was detected during the reaction. The molten mass was cooled, powdered, and triturated successively with caustic soda solution (10%) and water. The dried powder was then extracted twice with 50-ml portions of boiling ethanol and filtered after charcoal treatment. The filtrate on concentration furnished a light solid which was crystallized from an ethanol–water mixture (1:1) as white microcrystalline needles (2.1 g), mp 300–301° (λ_{max}^{EtOH} 255 mμ (log ε 4.22)).

Anal. Calcd for $C_{20}H_{16}N_4$: C, 76.9; H, 5.1; N, 17.9. Found: C, 76.7; H, 4.9; N, 17.5.

It was very weakly basic and did not afford any stable picrate or hydrochloride.

B.—The triazole IIa obtained in a yield of 6.9 g was also synthesized from IIIa (17 g, 0.066 mole), freshly distilled aniline (6.2 g, 0.067 mole), and fused zinc chloride (10 g, 0.07 mole) following the same procedure used in A. The mixture melting point with the sample of triazole prepared in the previous experiment showed no depression.

C.—A mixture of 2-anilino-5-phenylfuradiazole (7.1 g, 0.03 mole), freshly distilled aniline (2.8 g, 0.03 mole), and fused zinc chloride (10 g, 0.07 mole) following the same procedure as in A afforded IIa (3.2 g) which showed no depression upon mixture melting point with a sample of IIa prepared in the previous experiment.

The other triazoles shown in Table II were prepared by following procedure A.

The triazole IId was also prepared by the method B from IIIb. The triazole afforded picrate from ethanol in brownish yellow needles, mp 230° dec.

Anal. Calcd for $C_{19}H_{15}N_5$, $C_6H_3N_3O_7$: N, 22.7; Found: N, 22.2.

2-(4-Pyridyl)-1,3,4-oxadiazol-5-one (VII) and Symmetrical Diisonicotinylhydrazine (VI).—A mixture of isonicotinic acid hydrazide (27.2 g, 0.2 mole) and urethane (35.6 g, 0.4 mole) was heated for 6 hr in a flask fitted with an upright condenser in an oil bath at 150–160°. The cooled reaction mass after refluxing was treated with water (100 ml) and filtered, and the yellow residual solid (18 g) was triturated with ethanol (100 ml) and was filtered. The yellow solid left behind upon crystallization from water afforded VII as yellow needles (6 g), mp 266° dec (lit.[7] mp 266° dec). Mixture melting point with an authentic sample of VII showed no depression.

Removal of ethanol from the filtrate described above gave a solid which on crystallization from water yielded VI in white

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[9] In the Experimental Section the melting points are determined in capillary tubes using an electrical air bath and a silicon oil bath and are uncorrected. Microanalyses were performed at the microanalytical laboratory of the Bengal Immunity Research Institute.

[10] T. Vitali and S. Sardella, *Chimica* (Milan), **7**, 229 (1952); *Chem. Abstr.*, **47**, 6414 (1953).

TABLE II

Compd	Mp, °C	Formula	Calcd, % C	H	N	Found, % C	H	N
IIb	264–265	$C_{20}H_{14}N_4Cl_2$	62.9	3.7	14.4	62.6	3.8	14.8
IIc	232–233	$C_{20}H_{28}N_4$	74.1	8.6	17.3	74.2	8.5	17.3
IId	309–310 dec	$C_{19}H_{15}N_5$	72.8	4.9	22.4	72.6	4.8	22.5

needles 7 g, mp 263–264° (lit.[6] mp 264°). Mixture melting point with an authentic sample of VI remained undepressed.

Formation of Benzaldehyde (Va) from 1-Benzoylsemicarbazide (Ia).—An intimate mixture of Ia (18 g, 0.1 mole) and anhydrous sodium carbonate (22 g, 0.21 mole) was heated in a distilling flask in an atmosphere of carbon dioxide at 260–270° in an oil bath for 3 hr. A yellowish oil that distilled was collectd in an ice-cooled receiver, and the evolved gas, which had a definite smell of ammonia, wasp assed successively through sulfuric acid (10%) and potassium hydroxide solution (50%) and was finally collected in an aspirator by downward displacement of water.

The oil (2.5 g) was purified by distillation, bp 178–179° (760 mm) and was identified to be benzaldehyde through its 2,4-dinitrophenylhydrazone, mp 235–236°. Mixture melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of benzaldehyde showed no depression. The gas collected in the aspirator was qualitatively analyzed in a standard Orsat apparatus. Carbon dioxide was absorbed in potassium hydroxide (50%) solution. The trapped oxygen of the system was then absorbed in potassium pyrogallate solution (10 g of pyrogallol in 200 ml of 50% potassium hydroxide solution). Carbon monoxide was absorbed in ammoniacal cuprous chloride solution (23 g of cuprous chloride, 86 ml of liquor ammonia (29%, w/w), and 100 ml of water). The rest of the gas was found to be nitrogen. Under an analogous condition, Ib and Ic afforded *p*-chlorobenzaldehyde (Vb), (semicarbazone, mp 218–220° (lit.[11] mp 218–220°)) and isonicotinaldehyde (Vc) (characterized as its thiosemicarbazone, mp 220–222° (lit.[12] mp 221°), respectively.

Registry No.—Ia, 2845-79-6; Ib, 2845-81-0; Ic, 2845-80-9; Id, 15129-13-2; Ie, 3064-22-0; If, 2880-02-6; IIa, 15129-16-5; IIb, 15129-17-6; IIc, 15129-18-7; IId, 15215-85-7; IId picrate, 15128-81-1; IIIa, 1152-32-5; IIIb, 15152-50-8; Va, 100-52-7; Va 2,4-dinitrophenylhydrazone, 1157-84-2; VI, 4329-75-3; VII, 2845-82-1.

[11] F. Mayer and F. A. English, *Ann.*, **417**, 60 (1918).

[12] H. H. Fox, *J. Org. Chem.*, **17**, 555 (1952).

The Reductive Ring Cleavage of 1,3-Disubstituted Imidazolium Iodides by Sodium Borohydride

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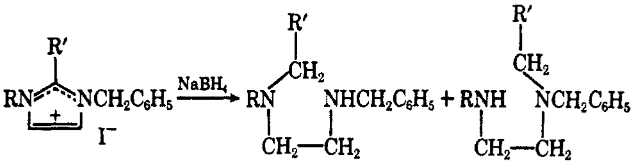
The use of sodium borohydride ($NaBH_4$) to effect reduction of heterocyclic quaternary salts is now a well-established and widely utilized procedure[1] leading to partially or totally reduced ring systems. Among the monocyclic nitrogenous systems having been investigated are pyridinium, pyrazinium, and thiazolium salts.

Our own interest in the imidazoles prompted the study of the effect of $NaBH_4$ on some simple, dissimilarly substituted imidazolium iodides of type I.

The preparation of quaternary salts Ia–e was carried out in acetonitrile and offered no unusual difficulties (see Table I). Aryl-containing substituents were chosen to facilitate isolation and characterization of the reaction products. In the imidazoles, entering quaternizing groups always come to reside on N-3. This fact, suggested by the observation of Sarasin[2] that thermal decomposition of the methiodide of 1-methyl-5-chloroimidazole gave 1-methyl-4-chloroimidazole, was proved unequivocally by nmr measurements on the dimethylimidazolium ion.[3] Our own work led us to note that the 1-methyl-3-benzylimidazolium iodide, prepared by the reaction of 1-methylimidazole with benzyl iodide, was identical with the salt obtained from 1-benzylimidazole and methyl iodide.

The reaction of the quaternary salts with $NaBH_4$ was carried out using a large excess of reducing agent in refluxing 95% alcohol; the hydrolyzed crude reaction mixtures were analyzed by vapor phase chromatography. In all cases examined reductive ring cleavage occurred, giving mixtures consisting of two isomers (93–99% of total) present in unequal amounts. Upon reducing Ia the major (85%) and minor (8%) components were identified as N,N-dimethyl-N′-benzylethylenediamine (IIa) and N,N′-dimethyl-N-benzylethylenediamine (IIIa) by comparing the chromatogram of the crude mixture with that of a mixture of authentic amines. From the reaction mixture, IIa was isolated by crystallization of the bishydrochloride salt which was identical with authentic material.



I II III

a, R = CH_3; R′ = H
b, R = C_2H_5; R′ = H
c, R = *n*-C_3H_7; R′ = H
d, R = CH_3; R′ = CH_3
e, R = C_2H_5; R′ = CH_3

Parallel behavior was noted upon reducing Ib–e. The major fraction produced from Ib was identical with the one isolated from Id and is, of necessity, N-methyl-N-ethyl-N′-benzylethylenediamine (IIb ≡ IId). Compound Ie gave the known N,N-diethyl-N′-benzylethylenediamine (IIe), whereas Ic, by analogy, furnished N-methyl-N-propyl-N′-benzylethylenediamine (IIc). In all cases separation of type II from III was carried out *via* the hydrochloride salts.

The postulated structures IIa–e were further substantiated by nmr data. Whereas types II and III could not be distinguished in D_2O, spectra in sulfuric acid clearly showed spin coupling with the NH^+ protons. In compound IIa the methyls are split into a

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[1] R. E. Lyle and P. S. Anderson, *Advan. Heterocyclic Chem.*, **6**, 50 (1966).

[2] J. Sarasin, *Helv. Chim. Acta*, **6**, 370 (1923).

[3] C. G. Overberger, J. C. Salamone, and S. Yaroslavsky, *J. Org. Chem.*, **30**, 3580 (1965).