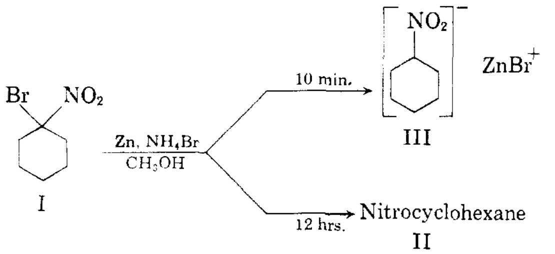


Reduction of 1-bromo-1-nitrocyclohexane (I) was then studied using an excess of zinc and ammonium bromide. In this case the only product isolated was cyclohexylamine hydrobromide (IV). When nitrocyclohexane is reduced under the same conditions cyclohexylamine hydrobromide is also formed. When, however, the reaction is stopped after only one hour, *N*-cyclohexylhydroxylamine (V) is formed as is reported in the literature.[2,3] The structure of the hydrobromide was confirmed by treatment with aqueous alkali and preparation of *N*-cyclohexylbenzamide (VI) from the resulting free amine.

EXPERIMENTAL

1-Bromo-1-nitrocyclohexane was prepared in 60% yield according to the procedure of Iffland and Criner.[4] Melting points and boiling points are uncorrected. Analyses by Mr. E. M. Hubbard and associates and by Galbraith Laboratories, Knoxville, Tenn.

Zinc reduction of 1-bromo-1-nitrocyclohexane (I), (*a*) *To nitrocyclohexane* (II). 1-Bromo-1-nitrocyclohexane (20.8 g., 0.10 mole) was mixed with 250 ml. of methanol and 17.6 g. (0.18 mole) of ammonium bromide, 11.6 g. of 90% zinc dust (0.16 mole) added and heating of the mixture begun. As in Klager's experiment, a white precipitate formed almost immediately with concomitant disappearance of the zinc dust. However, the reaction was not stopped at this point but allowed to reflux for 12 hr. further. At the end of the reaction a white solid was still present. After cooling, this solid was removed by filtration, washed with methanol, dried (Abderhalden), and analyzed.

Anal. Found: C, 0.70, 1.08; H, 2.46, 2.76; N, 9.35, 9.65; Br, 56.36, 56.53; Zn, 27.57, 27.87.

The filtrate was evaporated to small volume and the residue partitioned between ether and water. The ether solution was washed once with water, dried over sodium sulfate and evaporated to small volume. The residue was distilled yielding 5.7 g. (44.1%) of nitrocyclohexane, b.p. 16 mm. 88–90°, $n_D^{25^\circ}$ 1.4612.

Anal. Calcd. for $C_6H_{11}NO_2$: C, 55.79; H, 8.58. Found: C, 56.09; H, 8.69.

(*b*) *To cyclohexylamine hydrobromide* (IV). To a mixture of 14.5 g. (0.07 mole) of 1-bromo-1-nitrocyclohexane and 34 g. (0.35 mole) of ammonium bromide in 400 ml. of methanol was added 23.3 g. (0.32 mole) of 90% zinc dust in small portions. After the initial reaction had subsided, the mixture was heated at reflux for 16 hr. The mixture was filtered and the solvent evaporated. The residue was dissolved in cold methanol and filtered. Crystallization from ether-methanol afforded 3.0 g. (24%) of cyclohexylamine hydrobromide. Evaporation of the mother liquor afforded another 5.0 g. of crude material. A benzamide prepared in the usual way from the free amine[5] had a melting point of 148.5–149.3°, mixed melting point with an authentic sample of *N*-cyclohexylbenzamide, 148.5–149.2°.

Reduction of nitrocyclohexane. (*a*) *To N-cyclohexylhydroxylamine* (V). To a solution of 12.9 g. (0.10 mole) of nitrocyclohexane in 250 ml. of methanol was added 39.2 g. (0.40 mole) of ammonium bromide and 21.8 g. (0.30 mole) of 90% zinc dust. After the initial exothermic reaction had subsided the mixture was heated at reflux for 1 hr. The mixture was then filtered and the filtrate evaporated to dryness. The residue was dissolved in ether-methanol, the solution was filtered and crystallization effected from methanol-hexane. The crystals were filtered, washed with hexane and air dried yielding 7.0 g. (60.8%) of *N*-cyclohexylhydroxylamine, m.p. 136.5–138° with sublimation (lit.,[6] m.p. 137°).

(*b*) *To cyclohexylamine hydrobromide* (IV). To a solution of 6.45 g. (0.05 mole) of nitrocyclohexane in 150 ml. of methanol was added 29.4 g. (0.30 mole) of ammonium bromide and 13.1 g. (0.18 mole) of 90% zinc dust. After the initial exothermic reaction had subsided, the mixture was heated at reflux for 16 hr. The mixture was then filtered and the filtrate evaporated to dryness. The residue was redissolved in cold methanol, the solution filtered, and ether added to the filtrate. The resulting crystals were filtered, washed with ether and air dried yielding 4.12 g. (46%) of cyclohexylamine hydrobromide. The benzamide prepared from a portion of this sample had a melting point of 148–149° and when mixed with authentic *N*-cyclohexylbenzamide, a melting point of 148.2–149.2°.

RESEARCH AND ENGINEERING DIVISION
MONSANTO CHEMICAL COMPANY
DAYTON 7, OHIO

---

(3) J. Scheiber, *Ann.*, **365**, 215 (1909).

(4) D. C. Iffland and G. X. Criner, *J. Am. Chem. Soc.*, **75**, 4047 (1953).

(5) R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, 3rd Ed., New York (1948), p. 177.

(6) G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944).

Syntheses of 1-Benzylnaphthalenes

HUSSEIN A. FAHIM, ABDALLAH M. FLEIFEL, AND (MRS.) FAWZIA FAHIM

Received September 14, 1959

The syntheses of substituted 1-benzylnaphthalenes may be effected by the action of benzylmagnesium chloride solution on the corresponding tetralones. The tertiary alcohols, which, are the initial reaction products, are easily dehydrated by distillation in vacuum during purification to olefins (IIa–g), 3,4-dihydro-1-benzylnaphthalenes and/or the double bond isomers, 1-benzal-1,2,3,4-tetrahydronaphthalenes (*cf.* Howell and Robertson[1]). These may be dehydrogenated with sulfur to the corresponding 1-benzylnaphthalenes (IIIa–g) as shown in the following scheme:

---

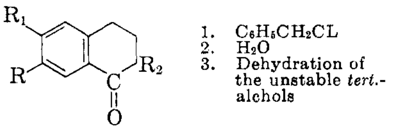
(1) W. N. Howell and A. Robertson, *J. Chem. Soc.*, 587 (1936).

TABLE I

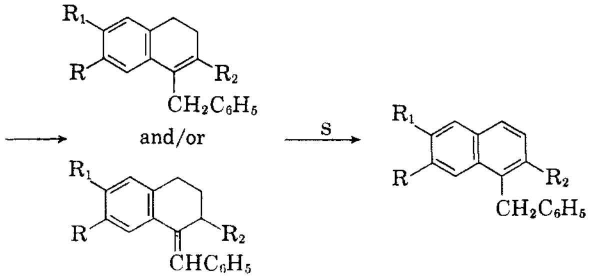
SUBSTITUTED 1-BENZYL-3,4-DIHYDRO- AND 1-BENZYL-NAPHTHALENES

Starting Material	Product	B.P.	M.P.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Ia[a]	IIa	181/183/8 mm.		70	$C_{17}H_{16}$	92.72	91.96	7.27	7.09
	IIIa	200–202/8 mm.	58	50	—	—	—	—	—
Ib[b]	IIb	190–192/8 mm.		51	$C_{18}H_{18}$	92.30	91.85	7.69	7.75
	IIIb	208–210/10 mm.	58–59	47	$C_{18}H_{16}$	93.10	92.50	6.89	6.80
Ic[c]	IIc	180–183/10 mm.		45	$C_{18}H_{18}O$	86.4	86.47	7.20	7.08
	IIIc	200–210/10 mm.	56–57	82	$C_{18}H_{16}O$	87.09	86.68	6.45	6.16
Id[d]	IId	218–220/10 mm.		65	$C_{17}H_{15}Br$[e]	68.22	68.80	5.01	4.87
	IIId	226–227/10 mm.	109–110	30	$C_{17}H_{13}Br$[f]	68.68	69.01	4.37	4.75
Ie[b]	IIe	200–202/10 mm.		48	$C_{19}H_{20}$	91.93	91.25	8.06	7.86
	IIIe	210–212/10 mm.	78–79	70	$C_{19}H_{18}$	92.68	91.85	7.31	7.24
If[g]	IIf	200–203/10 mm.		55	$C_{19}H_{20}$	91.93	91.15	8.06	7.85
	IIIf	208–210/10 mm.	96–97	75	$C_{19}H_{18}$	92.68	91.95	7.31	7.09
Ig[h]	IIg	206–207/10 mm.		65	$C_{19}H_{20}O_2$	81.43	80.95	7.14	7.11
	IIIg	245–247/10 mm.	94–95	80	$C_{19}H_{18}O_2$	82.01	81.79	6.47	6.25

[a] Ia, E. L. Martin and L. F. Fieser, *Org. Syntheses*, **Coll. Vol. II**, 569 (1950). [b] Ib, Ie, E. De Barry Barnett and F. G. Sanders, *J. Chem. Soc.*, 436 (1933). [c] Ic, P. C. Mitter and L. K. De, *J. Indian Chem. Soc.*, *16*, 35 (1939). [d] Id, L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, *60*, 170 (1938). [e] Calcd.: Br, 26.75; Found: 26.2. [f] Calcd.: Br, 26.96; Found: 27.32. [g] If, (*cf.* ref. 3). [h] Ig, R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 1485 (1932).



Ia. R = R_1 = R_2 = H
Ib. R = CH_3, R_1 = R_2 = H
Ic. R = OCH_3, R_1 = R_2 = H
Id. R = Br, R_1 = R_2 = H
Ie. R = R_1 = CH_3, R_2 = H
If. R = R_2 = CH_3, R_1 = H
Ig. R = R_1 = OCH_3, R_2 = H



II III

IIa. R = R_1 = R_2 = H
IIb. R = CH_3, R_1 = R_2 = H
IIc. R = OCH_3, R_1 = R_2 = H
IId. R = Br, R_1 = R_2 = H
IIe. R = R_1 = CH_3, R_2 = H
IIf. R = R_2 = CH_3, R_1 = H
IIg. R = R_1 = OCH_3, R_2 = H
IIIa. R = R_1 = R_2 = H
IIIb. R = CH_3, R_1 = R_2 = H
IIIc. R = OCH_3, R_1 = R_2 = H
IIId. R = Br, R_1 = R_2 = H
IIIe. R = R_1 = CH_3, R_2 = H
IIIf. R = R_2 = CH_3, R_1 = H
IIIg. R = R_1 = OCH_3, R_2 = H

An authentic specimen of IIIa was prepared by the Friedel-Crafts reaction, when naphthalene was allowed to react with benzyl chloride in the presence of anhydrous aluminum chloride as recommended by Nenitzescu *et al.*[2]

The products of the Grignard reaction (IIa–g) and substituted 1-benzylnaphthalenes (IIIa–g) are listed in Table I.

EXPERIMENTAL

General procedure. A solution of the tetralone (Ia–g, 0.1 mole) in dry thiophene-free benzene (25 ml.) was added to the Grignard solution of benzylmagnesium chloride (from benzyl chloride, 0.3 mole, magnesium metal, 0.4 g. 1.2 g.-atoms and dry ether 30 ml.). The mixture was refluxed on a steam bath for 3–5 hr. (Ia–e, Ig); (in the case of If, reflux period was 20 hr.) (*cf.* Baddar *et al.*[3]).

It was decomposed with cold dilute sulfuric acid, extracted with ether, dried over anhydrous sodium sulfate, the ether removed, and the product fractionally distilled in vacuum. The olefins (IIa–g) were oily materials which did not solidify and hence were purified by vacuum distillation (twice) in a ground-joint apparatus prior to analysis.[3]

Dehydrogenation. The olefin (IIa–g, 1 g.) was heated with sulfur (0.3 g.; 1.2 g.-atom) in a nitrobenzene bath (205–210°) for 5 hr. (except IId, 1 hr.) until hydrogen sulfide ceased to be evolved. The product was extracted with ether, filtered, dried, and the solvent evaporated. The residual oil was purified by distillation in vacuum and the solid obtained on cooling (IIIa–g) was crystallized from methanol.

Authentic 1-benzylnaphthalene (IIIa).[4] This was prepared according to Nenitzescu *et al.*[2] A mixture of naphthalene (20 g.) and benzyl chloride (6 g.) was treated portionwise with aluminum chloride (22 g.) until hydrogen chloride ceased to be evolved. The product was decomposed with 6*N* hydrochloric acid and steam distilled. The residue was taken up in ether, dried, distilled in vacuum at 200–202°/8 mm., and crystallized from ethanol, m.p. 58°, undepressed when mixed with IIIa.

CHEMISTRY DEPARTMENT
FACULTY OF SCIENCE
CAIRO UNIVERSITY
GIZA, CAIRO, EGYPT, U.A.R.

---

(2) C. D. Nenitzescu, D. A. Isăcescu, and C. N. Ionescu, *Ann.*, **491**, 217 (1931).

(3) F. G. Baddar, H. A. Fahim, and A. M. Fleifel, *J. Chem. Soc.*, 3302 (1955).

(4) I. I. Lapkin and A. V. Lyubimova, *J. Gen. Chem.*, 19, 707 (1949), gave m.p. 58° for 1-benzylnaphthalene which they prepared by Clemmensen reduction of 1-naphthylphenyl ketone.