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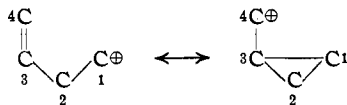
## The Diazotization of *o*-(1-Cycloalkenyl)-benzylamines. The Synthesis of Condensed Hydrocarbons

BY WILLIAM E. PARHAM, CHARLES D. WRIGHT<sup>1</sup> AND DONALD A. BOLON<sup>2</sup>

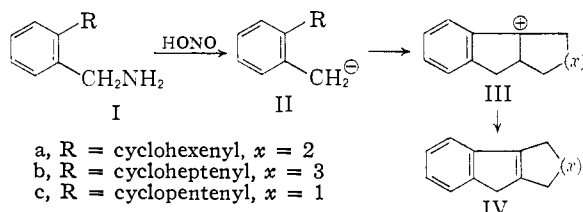
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A study of the diazotization of *o*-(1-cycloalkenyl)-benzylamines (I) in which the cycloalkenyl group was cyclohexenyl, cycloheptenyl and cyclopentenyl, has established that the aliphatic double bond, in these systems, can compete with the solvent water for the intermediate carbonium or diazonium ion. The order of competition is  $C_7 > C_6 \gg C_5$ . Separable mixtures of condensed hydrocarbon and *o*-(1-cycloalkenyl)-benzyl alcohol are obtained when the cycloalkenyl group is  $C_7$  and  $C_6$ ; however, no detectable hydrocarbon was obtained with the  $C_5$ -derivative. The corresponding  $C_7$  and  $C_6$  *o*-(1-cycloalkenyl)-benzyl alcohols afford high yields of condensed hydrocarbon by reaction with formic acid. A new synthesis of 1,2-benzazulene is described.

The formation of carbon-carbon bonds by diazotization of *endo*-2-amino- $\Delta^{5,6}$ -norbornene<sup>3,4</sup> and allylcarbinylamines<sup>5</sup> is well known, and is probably the consequence of interaction of an initially formed carbonium ion with a  $\beta$ -vinyl group. Simonetta and Winstein<sup>6</sup> have termed this 1,3-interaction homoallylic resonance, and their calculations show that when carbons 1 and 3 are in the most favorable position for interaction (interatomic distance 1.95 Å.) the stabilization is approximately 40% of that of the allyl carbonium ion.



It was of interest to determine whether unsaturated amines other than *beta* would yield cyclic products upon reaction with nitrous acid, and the *o*-(1-cycloalkenyl) system I, in which the cycloalkenyl ring was cyclopentenyl, cyclohexenyl or cyclo-



heptenyl, was chosen since: (1) the cationic center and the olefinic function would be in close proximity, (2) conversion of the primary benzyl cation II to the tertiary benzyl cation III could be energetically favorable, (3) and the products (IV) would be of considerable interest as intermediates to a variety of fused polycyclic systems (benzazulenes, benzpentalenes, etc.).

The reaction sequence used for the preparation of the *o*-(1-cycloalkenyl)-benzylamines (I) is shown in the following equations. Each step occurred in reasonably high yield; however, small amounts

(1) In part from the Ph.D. thesis of Charles D. Wright, University of Minnesota, 1956; Visking Fellow, 1954-1955.

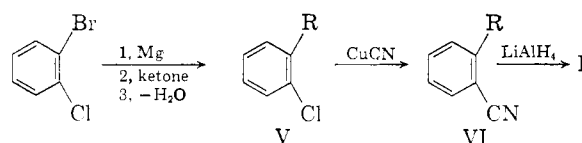
(2) In part from the Ph.D. thesis of Donald A. Bolon, University of Minnesota, 1960; Ethyl Corporation Fellow, 1958-1959; National Science Fellow, 1959-1960.

(3) W. E. Parham, W. T. Hunter and R. Hanson, *THIS JOURNAL*, **73**, 5068 (1951).

(4) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **77**, 3034 (1955).

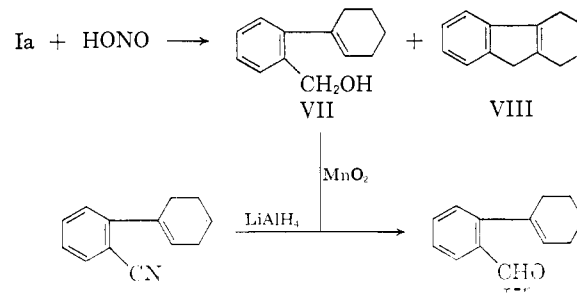
(5) J. D. Roberts and R. H. Mazur, *ibid.*, **72**, 3329 (1950).

(6) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).



of impurities present in V and VI were difficult to remove. The impurities,<sup>7</sup> believed to contain *o*-quaterphenyl in the cyclohexenyl example, were easily separated from the basic amines I, and in later experiments no extensive purification of V and VI was attempted, although the amines I were obtained in each case in high purity.

The diazotizations of Ia-c were carried out under identical conditions in aqueous solution. When the cycloalkenyl group was cyclohexenyl (Ia) two products were isolated by distillation: the alcohol VII and the hydrocarbon VIII. The yield of VI was estimated (isolation and refractive index) to be 34-55%, and the yield of hydrocarbon was similarly estimated to be 7-11%. The alcohol

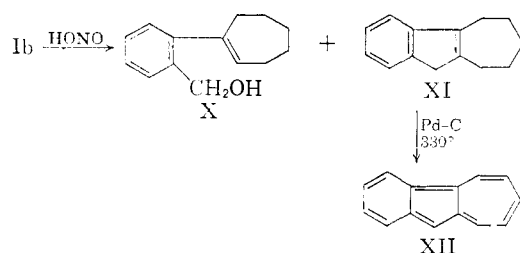


VII was further characterized by its conversion to *o*-(1-cyclohexenyl)-benzaldehyde (IX) which was identical with the product obtained by reduction of *o*-(1-cyclohexenyl)-benzonitrile with lithium aluminum hydride. The hydrocarbon VIII was characterized by its independent synthesis by the procedure previously reported by Colonge and Sibeud.<sup>8</sup>

When the cycloalkenyl group was cycloheptenyl (Ib) the product was composed of alcohol X and the hydrocarbon XI. The yields of X and XI were estimated (isolation, refractive index data and infrared analysis) to be nearly 50:50. The position of the double bond in XI was established by

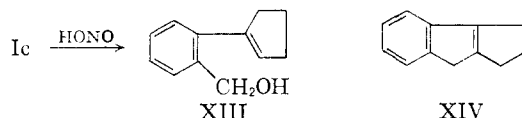
(7) A material, m.p. 116-117°, and believed to be *o*-quaterphenyl, was isolated by processing the neutral fraction obtained by reduction of crude VIa (see W. E. Bachman and H. T. Clarke, *ibid.*, **49**, 2089 (1927)).

(8) J. Colonge and J. Sibeud, *Bull. soc. chim. France*, **75** (1953).



nuclear magnetic resonance<sup>9</sup> (see Experimental), and XI was further characterized by its conversion to 1,2-benzazulene (8.7% yield) by dehydrogenation with palladium and charcoal. The benzazulene obtained melted at 175–176° dec. (reported<sup>10</sup> 176–177° dec.); however, the melting point was raised to 180–181° dec. by processing with phosphoric acid. The ultraviolet and visible spectra of the benzazulene thus obtained is compared in the Experimental section to the spectra reported by Nunn and Rapson<sup>10</sup> and by Braude and Forbes<sup>11</sup> for 1,2-benzazulene prepared by different synthetic procedures.

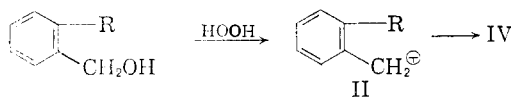
When the cycloalkenyl group of I was cyclopentenyl (Ic) no lower boiling component cor-



responding to the hydrocarbon XIV was evident. Although the product, obtained in 46% yield, was not obtained in a state of analytical purity, its properties, composition and infrared spectrum suggest that it is *o*-(1-cyclopentenyl)-benzyl alcohol (XIII).

The results obtained suggest that the aliphatic double bond in II can compete with the solvent water for reaction with the intermediate carbonium or diazonium ion, and that the order of competition is  $C_7 > C_6 \gg C_5$ .

It seemed likely that the alcohols VII, X and XIII could be converted to the hydrocarbons IV, if the carbonium ion II was formed reversibly. This was realized in high yield, when the cyclo-



alkenyl ring was cyclohexenyl and cycloheptenyl, by reaction of the alcohol with hot formic acid; however, only unidentified oxygen-containing oils were obtained when the cycloalkenyl ring was cyclopentenyl.

### Experimental

***o*-(1-Cyclohexenyl)-chlorobenzene.**—Cyclohexanone (98.14 g., 1.0 mole) was added with attendant cooling during a 50-min. period to the Grignard reagent, under nitrogen, prepared from magnesium (25.7 g., 1.06 moles), *o*-chlorobromobenzene (191.5 g., 1.0 mole) in diethyl ether (500 ml.). The mixture was left overnight at room temperature for 12 hours, heated to reflux for 30 min., and the cool solution

was treated with saturated ammonium chloride (125 ml.). The filtered solution was dried (MgSO<sub>4</sub>) and concentrated, and the residual *o*-(1-cyclohexanol)-chlorobenzene was dehydrated by reaction with 88% formic acid (200 ml.) at the reflux temperature for 1 hour. The resulting cooled solution was neutralized with aqueous potassium hydroxide, the organic layer was separated with petroleum ether (b.p. 60–68°, 50 ml.) which was then washed with aqueous sodium hydroxide (10%), dried (MgSO<sub>4</sub>) and concentrated. The residue was chromatographed on 500 g. of alumina using petroleum ether (b.p. 60–68°) as eluent. The oil obtained was fractionated affording 97.0 g. (50% yield) of *o*-(1-cyclohexenyl)-chlorobenzene, b.p. 77° (0.73 mm.),  $n_{25}^{25} \text{D}$  1.5582.

*Anal.* Calcd. for C<sub>12</sub>H<sub>13</sub>Cl: C, 74.80; H, 6.80. Found: C, 74.76; H, 6.68.

***o*-(1-Cyclohexenyl)-benzonitrile.**—*o*-(1-Cyclohexenyl)-chlorobenzene (19.3 g., 0.1 mole), cuprous cyanide (11.7 g., 0.13 mole) and anhydrous pyridine (25 ml.) were sealed in a Pyrex carius tube and the mixture was heated in a furnace for 21 hours at 240 ± 4°. The tube was cooled and opened; the mixture was melted and poured into 250 ml. of 3 *N* ammonium hydroxide. The tube was washed with warm pyridine and 50:50 benzene-petroleum ether mixture. The rinses were added to the ammonium hydroxide solution which was filtered through two layers of toweling. The organic layer was separated and the aqueous solution was extracted with three 100-ml. portions of benzene-petroleum ether (50:50), a second filtration was necessary after the first extraction. The extracts were washed with two 100-ml. portions of dilute ammonium hydroxide, two 100-ml. portions of hydrochloric acid, and two 40-ml. portions of saturated aqueous sodium chloride. The organic layer was concentrated and distilled and there was obtained 5.18 g. of recovered *o*-(1-cyclohexenyl)-chlorobenzene and 8.6 g. (60% yield,  $n_{25}^{25} \text{D}$  1.5646) of *o*-(1-cyclohexenyl)-benzonitrile. To obtain a sample for analysis the product was (a) chromatographed on alumina using petroleum ether (b.p. 60–68°) as eluent, and (b) fractionally distilled (b.p. 92–94° (0.05 mm.),  $n_{25}^{25} \text{D}$  1.5648).

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>N: C, 85.20; H, 7.15; N, 7.64. Found: C, 85.24; H, 7.37; N, 7.81.

***o*-(1-Cyclohexenyl)-benzylamine.**—A solution of *o*-(1-cyclohexenyl)-benzonitrile (15.4 g., 0.084 mole,  $n_{25}^{25} \text{D}$  1.5651–1.5653) in ether was added to a cooled slurry of lithium aluminum hydride (3.5 g., 0.092 mole) in dry ether (175 ml.) maintained under a nitrogen atmosphere. The mixture was heated at the reflux temperature for 1 hour and was hydrolyzed by the addition of water (4 ml.), aqueous sodium hydroxide (20%, 2.6 ml.) and water (9.5 ml.) with attendant cooling. The ether solution was dried (MgSO<sub>4</sub>), and saturated ethereal hydrogen chloride was added until precipitation ceased. The hydrochloride of *o*-(1-cyclohexenyl)-benzylamine (14.04, 84% yield, m.p. 196–205° dec.) was obtained as a white solid which melted at 210–213° dec., after further recrystallization from dry ethanol-ether.

*Anal.* Calcd. for C<sub>13</sub>H<sub>15</sub>N: C, 69.79; H, 8.16; N, 6.26. Found: C, 69.54; H, 8.30; N, 6.21.

By concentrating the ethereal solution, from which the hydrochloride was separated, there was obtained an oily solid which melted at 100–108° after recrystallization from either acetonitrile or alcohol-water. The amount of neutral product obtained was dependent upon the degree of purification of the starting nitrile (2.6 g. of crude oily solid from a typical unchromatographed sample of nitrile). This material was assumed to be *o*-quaterphenyl (reported<sup>4</sup> m.p. 116–117°). A sample of this material melted at 113–115° after fractional sublimation (100° (0.1 mm.)).

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>: C, 94.08; H, 5.92. Found: C, 94.00; H, 5.92.

**Reaction of *o*-(1-Cyclohexenyl)-benzylamine Hydrochloride with Nitrous Acid.**—A mixture of *o*-(1-cyclohexenyl)-benzylamine hydrochloride (5.17 g., 0.023 mole), sodium nitrite (1.93 g., 0.028 mole) and distilled water (70 ml.) was heated for 2 hours on a steam-bath. The reaction mixture was cooled, and extracted with ether, and the ether extract was washed with dilute hydrochloric acid, dilute sodium hydroxide and finally with water. The ether extract was dried (MgSO<sub>4</sub>) and concentrated leaving 3.84 g. (83% calcd. as *o*-(1-cyclohexenyl)-benzyl alcohol) of a deep

(9) The authors wish to express their appreciation to Dr. George V. Tiers of Minnesota Mining and Manufacturing Co., for this analysis.

(10) J. R. Nunn and W. S. Rapson, *J. Chem. Soc.*, 825 (1949).

(11) E. A. Braude and W. F. Forbes, *ibid.*, 2210 (1953).

red oil. This oil contained two principal products which were separated by fractionation: (1) 1,2,3,4-tetrahydrofluorene (b.p.  $\sim 89^\circ$  (0.15 mm.), waxy solid) and (2) *o*-(1-cyclohexenyl)-benzyl alcohol (b.p.  $95^\circ$  (0.18 mm.),  $n_D^{25}$  1.5634). The yield of 1,2,3,4-tetrahydrofluorene was estimated by isolation and refractive index data to be 7–11%. The yield of *o*-(1-cyclohexenyl)-benzyl alcohol was similarly estimated to be a minimum of 55%.

**1,2,3,4-Tetrahydrofluorene.**—The waxy solid was purified by chromatography (alumina, using petroleum ether, b.p.  $60$ – $68^\circ$ , as eluent), and melted, after recrystallization from ethanol-water, at  $53.5$ – $55^\circ$ .

*Anal.* Calcd. for  $C_{13}H_{14}$ : C, 91.71; H, 8.29. Found: C, 92.03; H, 8.59.

This product was identical (mixed melting point and infrared spectrum) with a sample of 1,2,3,4-tetrahydrofluorene prepared as described by Colonge and Sibeud.<sup>8</sup>

*o*-(1-Cyclohexenyl)-benzyl alcohol was isolated by distillation; b.p.  $95^\circ$  (0.18 mm.),  $n_D^{25}$  1.5634. *Anal.* Calcd. for  $C_{13}H_{16}O$ : C, 82.93; H, 8.57. Found: C, 82.96; H, 8.76. It was characterized by its conversion to *o*-(1-cyclohexenyl)-benzaldehyde.

**1,2,3,4-Tetrahydrofluorene.**—A solution of pure *o*-(1-cyclohexenyl)-benzyl alcohol (0.876 g., 0.0465 mole) in formic acid (88%, 15 ml.) was heated for 75 minutes on a steam-bath. The mixture was cooled to  $0^\circ$ , and the crystalline solid was collected, washed with water, dried, and chromatographed on alumina using petroleum ether as eluent. 1,2,3,4-Tetrahydrofluorene (0.421 g., 53% yield, m.p.  $52$ – $54^\circ$ , m.p.  $56$ – $57^\circ$  from ethanol; less pure oily crystals (0.164 g.) were not processed) thus obtained was identical (m.p., mixture m.p.) with authentic 1,2,3,4-tetrahydrofluorene prepared by the method of Colonge and Sibeud.<sup>8</sup> The picrate of 1,2,3,4-tetrahydrofluorene prepared by both procedures melted at  $72^\circ$  (mixture m.p.  $72^\circ$ ).

#### *o*-(1-Cyclohexenyl)-benzaldehyde

1. From *o*-(1-Cyclohexenyl)-benzyl Alcohol.—The oxidation of VII (1.25 g., 0.066 mole) with activated manganese dioxide was carried out in ether (15 ml.) by the general procedure described by Harfenist, Baveley and Lazier.<sup>12</sup> The *o*-(1-cyclohexenyl)-benzaldehyde (0.65 g., 53% yield,  $n_D^{25}$  1.5732–1.5703) was isolated by distillation;  $n_D^{25}$  1.5709.

*Anal.* Calcd. for  $C_{11}H_{14}O$ : C, 83.83; H, 7.58. Found: C, 83.97; H, 7.60.

The oxime (m.p.  $110.5$ – $112^\circ$ ) was prepared in the usual manner from hydroxylamine, the aldehyde and pyridine, and was recrystallized from benzene-petroleum ether (b.p.  $30$ – $60^\circ$ ).

*Anal.* Calcd. for  $C_{11}H_{13}NO$ : C, 77.58; H, 7.51; N, 6.96. Found: C, 77.76; H, 7.61; N, 6.97.

The semicarbazone (m.p.  $212.5$ – $214^\circ$ ) was recrystallized from ethanol-water.

*Anal.* Calcd. for  $C_{14}H_{17}N_3O$ : C, 69.11; H, 7.04; N, 17.27. Found: C, 69.13; H, 7.22, 7.20; N, 16.60, 18.80.

2. From *o*-(1-Cyclohexenyl)-benzonitrile.—A slurry of lithium aluminum hydride (0.26 g., 0.007 mole) in absolute ether was added dropwise (1 hr.) to a cooled solution of *o*-(1-cyclohexenyl)-benzonitrile (4.27 g., 0.233 mole) in 70 ml. of ether under nitrogen. The mixture was stirred for 1 hour at room temperature, and was then treated with water (0.6 ml.), aqueous sodium hydroxide (20%, 0.3 ml.) and water (0.6 ml.). The ether was separated, washed successively with water, dilute hydrochloric acid, dilute sodium hydroxide and water. *o*-(1-Cyclohexenyl)-benzaldehyde ( $n_D^{25}$  1.5722) was obtained from the ether extract by distillation. The oxime (m.p.  $110$ – $111^\circ$ ) and semicarbazone (m.p.  $212$ – $214^\circ$  dec.) of this product caused no depression in melting point when admixed with the corresponding derivative prepared in 1, above.

*o*-(1-Cycloheptenyl)-chlorobenzene.—The Grignard reaction employing *o*-chlorobromobenzene (95.7 g., 0.5 mole), dry ether (250 ml.), magnesium (12.2 g., 0.5 g. atom) and cycloheptanone (56.6 g., 0.5 mole) was carried out essentially as described for the synthesis of *o*-(1-cyclohexenyl)-chlorobenzene. The mixture was hydrolyzed by a slurry of concentrated sulfuric acid (28 ml.) and ice instead of am-

monium chloride. The crude product was concentrated to remove solvent and some unreacted starting material; however, concentration was discontinued when the pot temperature reached  $160^\circ$  (0.25 mm.) (decomposition was noted). The viscous residue (76 g., 68% calculated as *o*-(1-cycloheptanol)-chlorobenzene) was dehydrated as described for the dehydration of *o*-(1-cyclohexanol)-chlorobenzene, and crude *o*-(1-cycloheptenyl)-chlorobenzene was obtained by distillation as a yellowish oil (b.p.  $71$ – $74^\circ$  (0.1 mm.),  $n_D^{25}$  1.5594, 52.9 g., 51% yield based on *o*-chlorobromobenzene).

This material was employed in the next step; however, a sample (5.6 g.) was chromatographed (alumina, 200 g.), using petroleum ether (b.p.  $60$ – $68^\circ$ ) as eluent and redistilled (b.p.  $153$ – $154^\circ$  (20 mm.),  $n_D^{25}$  1.5574) for analysis.

*Anal.* Calcd. for  $C_{13}H_{13}Cl$ : C, 75.17; H, 7.28. Found: C, 75.36, 75.67; H, 7.63, 7.42.

*o*-(1-Cycloheptenyl)-benzylamine Hydrochloride.—*o*-(1-Cycloheptenyl)-chlorobenzene (20.7 g., 0.1 mole,  $n_D^{25}$  1.5594) was treated with cuprous cyanide (11.7 g., 0.13 mole) for 48 hours at  $256^\circ$ , and the resulting mixture was processed as described for *o*-(1-cyclohexenyl)-benzonitrile. In addition to recovered *o*-(1-cycloheptenyl)-chlorobenzene (2.1 g., 10%) there was obtained 9.2 g. (b.p.  $85$ – $95^\circ$  (0.2 mm.), 46% yield,  $n_D^{25}$  1.5644) of impure *o*-(1-cycloheptenyl)-benzonitrile as a yellow oil.

Crude *o*-(1-cycloheptenyl)-benzonitrile (17.9 g., 0.091 mole,  $n_D^{25}$  1.5644) was reduced with lithium aluminum hydride (4.0 g., 0.105 mole), and the reaction mixture was processed as described for the preparation of Ia. The crude, grayish-white hydrochloride of *o*-(1-cycloheptenyl)-benzylamine was collected and dried in vacuum over sulfuric acid. The yield was 21.0 g. (89%, m.p.  $196$ – $200^\circ$  dec.), and the product was obtained as fine white needles, m.p.  $198$ – $200^\circ$  dec., from ethanol-ether.

*Anal.* Calcd. for  $C_{14}H_{20}NCl$ : C, 70.74; H, 8.42; N, 5.89. Found: C, 70.55; H, 8.25; N, 5.66.

Reactions of *o*-(1-Cycloheptenyl)-benzylamine Hydrochloride with Sodium Nitrite.—A mixture of *o*-(1-cycloheptenyl)-benzylamine hydrochloride (7.9 g., 0.033 mole), freshly distilled water (100 ml.) and sodium nitrite (2.80 g., 0.04 mole) in distilled water (20 ml.), under nitrogen, was stirred for 30 min. at  $30^\circ$ , and 60 min. at  $60^\circ$ . Ether (100 ml.) was added to the cooled mixture, and the ether extract was washed successively with hydrochloric acid (3 *N*), sodium hydroxide (5%) and water. The ether extract was dried ( $MgSO_4$ ) and fractionated (8" spiral wire column), and three combined fractions were collected: (1) b.p.  $103$ – $110^\circ$  (0.2 mm.), 1.39 g.,  $n_D^{25}$  1.5802; (2) b.p.  $110$ – $127^\circ$  (0.2 mm.), 0.95 g.,  $n_D^{25}$  1.5728; (3) b.p.  $110$ – $115^\circ$  (0.05 mm.), 1.25 g.,  $n_D^{25}$  1.5665–1.5680. Fraction 3 was essentially pure *o*-(1-cycloheptenyl)-benzyl alcohol.

*Anal.* Calcd. for  $C_{14}H_{18}O$ : C, 83.17; H, 8.91. Found: C, 82.93; H, 8.80.

Pure 3,4,5,6,7,8-hexahydro-1,2-benzazulene shows absorption at 719 and 1404  $cm^{-1}$  (see next section).

Analysis of fractions 1 ( $\sim 100\%$ ), 2 (45%) and 3 (0%) by this method indicated the yield of XI to be 54% and the yield of X to be 46%. These values compare with estimates of composition on the combined distillate (a different run) of 40 or 52% XI/60 or 48% X (infrared analysis depending upon wave lengths chosen for analysis), and 55–75% XI/25–45% X (plots of refractive index).

**3,4,5,6,7,8-Hexahydro-1,2-benzazulene.**—A solution of *o*-(1-cycloheptenyl)-benzyl alcohol (0.73 g., 0.00037 mole,  $n_D^{25}$  1.5665) in formic acid (88%, 15 ml.) was heated on a steam-bath for 2 hours. The mixture was cooled ( $0^\circ$ ) and the solid was collected by filtration, washed with water, and dissolved in petroleum ether ( $60$ – $68^\circ$ ). The solution was placed on a 12 cm.  $\times$  10 mm. column of alumina. The oily product which was eluted with petroleum ether (b.p.  $60$ – $68^\circ$ ) slowly crystallized (m.p.  $40$ – $47^\circ$ ) and melted at  $49$ – $50^\circ$  when recrystallized from ethanol-water or  $50.5$ – $51.5^\circ$  when sublimed ( $30^\circ$  (0.1 mm.); ultraviolet spectrum (*n*-heptane):  $\lambda$  260  $m\mu$ ,  $\log E_{max}$  4.16;  $\lambda$  216  $m\mu$ ,  $\log E_{max}$  4.14; infrared spectrum: 719 and 1404  $cm^{-1}$  used for analyses; refractive index  $n_D^{25}$  1.5673, estimate at  $25^\circ$  1.5778; n.m.r. spectrum<sup>9</sup> ( $\tau$  values from a 10% solution of XII in  $CCl_4$ ): 2.90 (aromatic), 6.80 (allylic  $CH_2$ -C<sub>1</sub> ring), 7.47 (allylic  $CH_2$ -C<sub>7</sub> ring), 8.21 (methylene  $CH_2$ -C<sub>7</sub>

(12) M. Harfenist, A. Baveley and W. Lazier, *J. Org. Chem.*, **19**, 1608 (1954).

TABLE I

A, <sup>a</sup> m $\mu$	B, <sup>b</sup> m $\mu$	C <sup>c</sup>	
		m $\mu$	log $E_{\max}$
382	..	382	3.29
365	..	360	3.21
341	..	343	2.81
323 <sup>d</sup>	..	318 <sup>d</sup>	4.20
300	..	297	4.60
..	..	251	4.29
..	516	525	1.62
560	565	568	1.74
625	615	618	1.76
660	660	655 <sup>d</sup>	
680	682	682	1.61
..	..	745	1.05
..	790	777	1.05

<sup>a</sup> A, pentane; I. R. Nunn and W. S. Rapson.<sup>10</sup> <sup>b</sup> B, pentane; E. A. Braude and W. F. Forbes.<sup>11</sup> <sup>c</sup> C, this study; ultraviolet—ethanol, visible—pentane, no reported peak. <sup>d</sup> Shoulder.

ring). The absence of absorbance between 2.90 and 6.80 indicates no vinyl hydrogen.

*Anal.* Calcd. for C<sub>14</sub>H<sub>16</sub>: C, 91.30; H, 8.70. Found: C, 91.15; H, 8.70.

**1,2-Benzazulene.**—The apparatus described by Anderson, Nelson and Tazuma<sup>13</sup> was used with the following modifications. A capillary micro dropping funnel with provision for positive nitrogen pressure was fitted in the top of the column. A flow rate of dry nitrogen at 0.5 ml./sec. was maintained. The 30-cm. vertical column was packed with 2.5% Pd-asbestos. The receiver was cooled (Dry Ice-acetone) and a vacuum of 60 mm. was applied to the column.

**3,4,5,6,7,8-Hexahydro-1,2-benzazulene** (0.69 g., 0.00038 mole), kept liquid by an infrared lamp, was added at the rate of one capillary drop every 10 minutes to the column heated to a stable temperature of 330° top, 310° bottom (addition time 8 hours). The product was dissolved in petroleum ether (30–60°) and chromatographed on alumina. Fraction 1, bluish crystals, was mostly recovered XII; fractions 2 and 3, dark green plates, melted at 175–177° dec. 1,2-Benzazulene is reported to melt at 176–177° dec.

The three fractions were dissolved in petroleum ether (b.p. 30–60°) and extracted three times with 85% phosphoric acid. The acid extract was added to ice (200 g.), and the resulting solution was extracted with ether. The ether extract was washed with 5% aqueous potassium carbonate, dried (MgSO<sub>4</sub>) and concentrated affording green

(13) A. G. Anderson, J. A. Nelson and J. J. Tazuma, *THIS JOURNAL*, **75**, 4980 (1953).

plates of 1,2-benzazulene (0.058 g., 8.7%, m.p. 180–181° dec.). The results of visible and ultraviolet spectra of 1,2-benzazulene are given in Table I. The general shape of the curves is quite similar to that reported by Nunn and Rapson.<sup>10</sup>

***o*-(1-Cyclopentenyl)-benzylamine Hydrochloride.**—The procedure employed was essentially identical with that described for the syntheses of VIIa. Since it was known that impurities and side products formed in these reactions were difficult to remove at steps prior to the formation of the basic amine, no rigorous purifications of intermediates were attempted.

From *o*-chlorobromobenzene (95.7 g., 0.5 mole), magnesium (12.2 g., 0.5 g. atom), cyclopentanone (42.1 g., 0.5 mole) and formic acid (88%, 110 ml.) there was obtained 51 g. (57% yield) of *o*-(1-cyclopentenyl)-chlorobenzene, b.p. 63–64° (0.15 mm.),  $n_{25}^D$  1.5716. From crude Vc (14.9 g., 0.1 mole) and cuprous cyanide (11.7 g., 0.13 mole) after 36 hours at 250°, there was obtained 6.8 g. (46%) of crude *o*-(1-cyclopentenyl)-benzimidazole, b.p. 106–110° (0.7 mm.),  $n_{25}^D$  1.5806. From *o*-(1-cyclopentenyl)-benzimidazole (14.4 g., 0.085 mole) and lithium aluminum hydride (3.5 g., 0.092 mole) there was obtained *o*-(1-cyclopentenyl)-benzylamine hydrochloride (white plates, m.p. 176–180° dec., 15.5 g., 87% yield). This material was recrystallized from absolute ethanol-ether and the pure amine hydrochloride was obtained as fine white crystals (m.p. 178° dec.).

*Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>NCl: C, 68.74; H, 7.64; N, 6.68. Found: C, 68.67; H, 7.57; N, 6.65.

**Reaction of *o*-(1-Cyclopentenyl)-benzylamine Hydrochloride with Nitrous Acid.**—*o*-(1-Cyclopentenyl)-benzylamine hydrochloride (5.0 g., 0.024 mole) was treated with sodium nitrite (2.1 g.) in water (60 ml.) as previously described for Ia and Ib. The product was fractionated through an 8" spiral wire column and only one component appeared to be present in any significant amount; b.p. 78–82° (0.08 mm.),  $n_{25}^D$  1.5746, 1.88 g., 46% yield calculated as *o*-(1-cyclopentenyl)-benzyl alcohol. The material was re-fractionated and samples showed essentially no variation in boiling point or refractive index.

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O: C, 82.76; H, 8.05. Found: C, 81.41, 80.79, 82.04; H, 8.09, 7.99, 8.66.

Attempts to cyclize the assumed *o*-(1-cyclopentenyl)-benzyl alcohol to 3,4,5,6-tetrahydro-1,2-benzazulene, by procedures essentially identical to those described for reactions involving VII and XII, were unsuccessful. The tarry products that resulted were extracted with petroleum ether and chromatographed on alumina as previously described. Only traces of oils resulted that could not be induced to crystallize. In one run (out of four) a small amount of solid (m.p. 58–62°) was obtained by recrystallization of the small amount of oil obtained from the chromatogram. This material was very sensitive to air and decomposed within minutes to an oil.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL., AND THE DEPARTMENT OF CHEMISTRY, QUEEN MARY COLLEGE, UNIVERSITY OF LONDON, LONDON E 1, ENG.]

## New Heteroaromatic Compounds. Part X.<sup>1</sup> Grignard Reactions and Hydride Reductions of B-Oxides Derived from 10,9-Borazarophenanthrene and 2,1-Borazonaphthalene<sup>2</sup>

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Grignard reagents reacted with 2,1-borazaro-2-naphthyl ethers to give 2-methyl- and 2-phenyl-2,1-borazonaphthalene while lithium aluminum hydride gave 2,1-borazonaphthalene. Similar reactions with 10-hydroxy-10,9-borazarophenanthrene gave 10-methyl-10,9-borazarophenanthrene and 10,9-borazarophenanthrene. The yields in all these reactions were good. The preparation of the necessary ethers is described.

Previous papers,<sup>3,4</sup> in this series have described the preparation of derivatives of the novel aro-

(1) Preceding paper, P. M. Maitlis, *J. Chem. Soc.*, in press.

(2) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960; Abstracts of Papers, p. 64-P.

matic compounds 10,9-borazarophenanthrene (I) and 2,1-borazonaphthalene (II). The B-alkyl and aryl derivatives, and the parent compounds

(3) M. J. S. Dewar, Ved P. Kubba and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

(4) M. J. S. Dewar and R. Dietz, *ibid.*, 2728 (1959).