

## Reactions of Conjugated Arylazocyclohexenes with Grignard Reagents; X-Ray Crystal Structure of 1-Hydroperoxy-1-(*o*-methoxyphenylazo)-2-phenylcyclohexane

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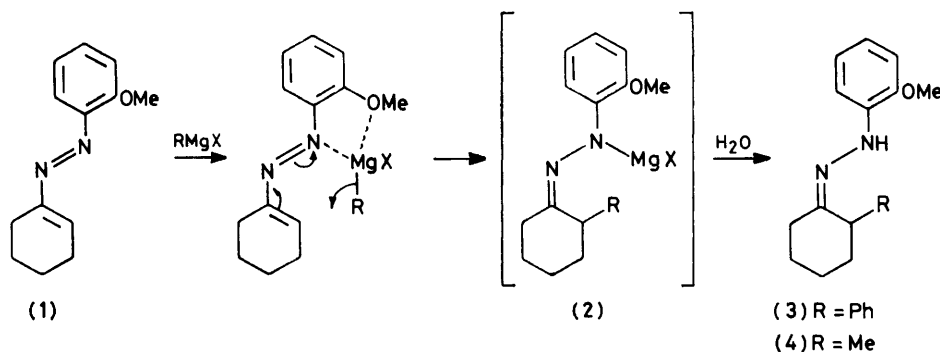
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Conjugated arylazocyclohexenes react with aromatic and aliphatic Grignard reagents to furnish 2-aryl- and 2-alkyl-cyclohexanone arylhydrazones having the *syn*-configuration with the 2-substituent axially oriented. Their structures have been established by chemical and spectroscopic methods. These compounds, as well as the *anti*-isomers, undergo ready autoxidation to give arylazo-hydroperoxides. The structure of 1-hydroperoxy-1-(*o*-methoxyphenylazo)-2-phenylcyclohexane has been determined by X-ray analysis.

We have shown previously that the reactions of *ortho*-substituted azobenzenes with arylmagnesium bromides result in aromatic arylation at free positions *ortho* to the azo-group.<sup>1</sup> The mechanism was shown to involve 1,4-addition (across the azo-group) followed by elimination of magnesium bromohydride.<sup>2</sup> In the case of *o*-methoxyazobenzene the aromatic arylation takes place *via* an intermediate complex in which the magnesium atom is co-ordinated to both the oxygen atom of the methoxy-group and the nitrogen atom linked to the

in the case of aromatic azo-compounds could be postulated, involving the intermediates (2) (Scheme 1).

Since azoalkanes display a higher reactivity than azobenzenes towards Grignard reagents,<sup>1</sup> we wished to discover whether the reaction takes place without the assistance of the *ortho*-methoxy-group. From the reactions of 1-phenylazocyclohexene (7)<sup>3</sup> with Grignard reagents under the same conditions, the hydrazone derivatives (5) and (6) were obtained in *ca.* 75% yield. However, with the Grignard reagents in large excess



SCHEME 1

substituted ring. No aromatic alkylation of *ortho*-substituted azobenzenes occurred with aliphatic Grignard reagents. By reductive cleavage at the azo-bridge, the arylation products furnished the corresponding *ortho*-aryl aromatic amines.

In the hope of extending this arylation and possible alkylation method to aliphatic and/or alicyclic compounds, we have investigated the reactions of conjugated arylazocyclohexenes with both aromatic and aliphatic Grignard reagents. Phenylmagnesium bromide and methylmagnesium iodide reacted with 1-(*o*-methoxyphenylazo)cyclohexene (1) giving, after hydrolysis, the corresponding 2-phenyl- and 2-methyl-cyclohexanone *o*-methoxyphenylhydrazones (3) and (4) in quantitative yield. The same reaction mechanism as that invoked

(4 mol. equiv.) quantitative yields of products were obtained. On the basis of this result, the reactivity of the phenylazo-compound (7) is not much less than that of the *o*-methoxy-derivative (1), and the co-ordination of the magnesium with the oxygen atom of the methoxy-group is not indispensable.

In order to show that attack of the group R had occurred at C-2 of the alicyclic system (Scheme 1), reductive cleavage of compounds (3)—(6) was carried out by hydrogenation over Raney nickel T-1.<sup>4</sup> The product mixtures were analysed by comparison with authentic samples. Compounds (3)—(6) all afforded mixtures of 2-substituted *cis*- and *trans*-cyclohexylamines together with the corresponding aromatic amine, *i.e.* *o*-anisidine or aniline.

The hydrazone structure of compounds (3)—(6) was

<sup>1</sup> A. Risaliti and S. Bozzini, *Ann. Chim. (Italy)*, 1964, **54**, 685; A. Risaliti and A. Stener, *ibid.*, 1967, **57**, 3; S. Bozzini and A. Stener, *ibid.*, 1968, **58**, 169.

<sup>2</sup> A. Risaliti, S. Bozzini, and A. Stener, *Tetrahedron*, 1968, **25**, 143; 1970, **26**, 3927.

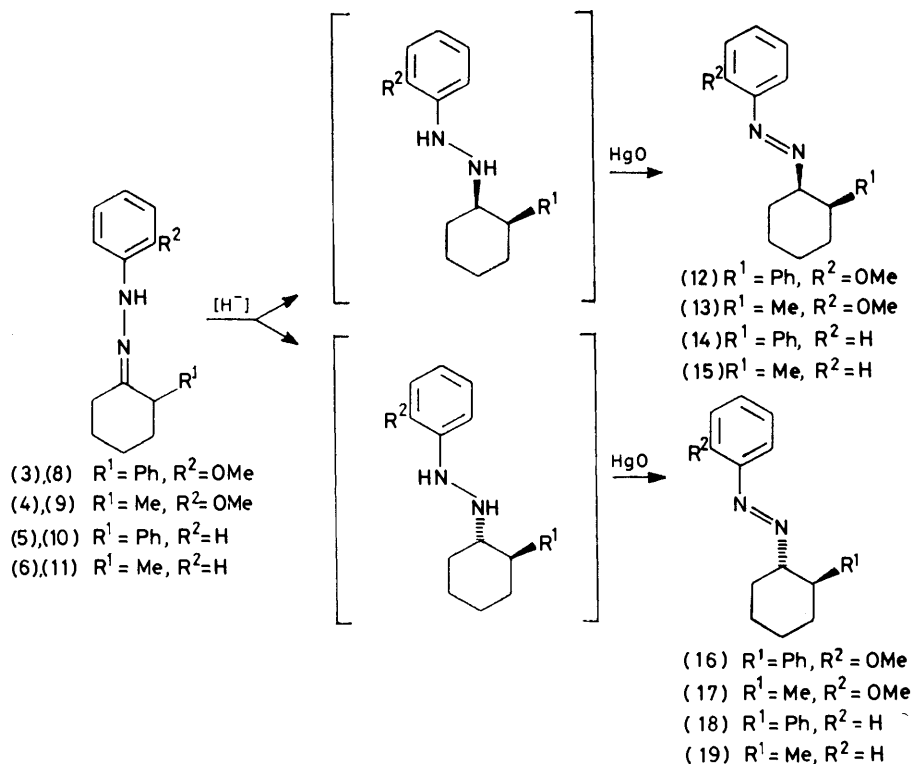
<sup>3</sup> S. Brodka and H. Simon, *Chem. Ber.*, 1969, **102**, 3647.

<sup>4</sup> X. A. Dominguez, I. C. Lopez, and R. Franco, *J. Org. Chem.*, 1961, **26**, 1625.

determined by reduction to the corresponding hydrazine derivatives and oxidation of these to azo-compounds, (12)—(19). Reduction was carried out with borohydride and oxidation by mercury(II) oxide, without isolating the hydrazine derivatives, owing to their instability (Scheme 2).

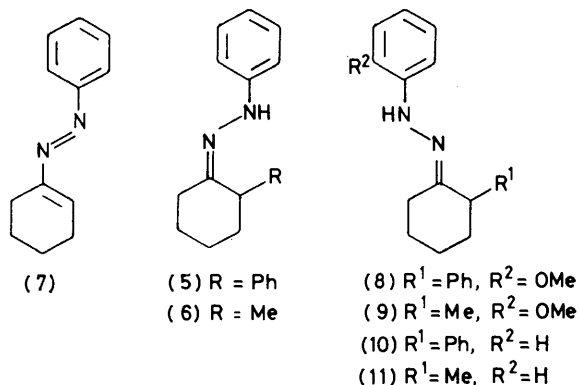
According to the postulated reaction mechanism, the

be different. Conformation (a) with R equatorially oriented should be the most favoured for the *anti*-isomers. In the analogous conformation (b) of the *syn*-derivatives a strong  $A^{(1,3)}$  allylic strain<sup>5,6</sup> between R and NHAr is operative and therefore the conformational equilibrium is almost completely shifted towards the form (c). As a consequence a difference in behaviour was expected in



SCHEME 2

hydrazone compounds (3)—(6) should have the *syn*-configuration. In fact the products are isomeric with the corresponding *anti*-hydrazones (8)—(11), obtained by



synthesis from 2-phenyl- and 2-methyl-cyclohexanone and the appropriate hydrazines.

The conformational features of the two series of hydrazones (3)—(6) and (8)—(11) would be expected to

reductions of the C=N double bond of compounds (3)—(6) and (8)—(11), owing to the different orientation of the substituent R. In fact attack of the reductive reagent could occur from either side of the molecule in conformation (a), whereas in conformation (c) attack from the side of the axial R group would be hindered. Nevertheless, reductive cleavage of both *syn*- and *anti*-isomers led to mixtures of the corresponding *cis*- and *trans*-cyclohexylamines in about the same ratio in each case.

However significant stereoselectivity was found in the reduction-oxidation reactions of the hydrazones (3)—(6) and (8)—(11). The *syn*-isomers gave almost exclusively the corresponding *cis*-azo-compounds, whereas the *anti*-isomers furnished a mixture of *cis*- and *trans*-azo-compounds in about the same ratio in each case.

The *cis*- and *trans*-configurations of the azo-compounds (12)—(19) were established by reductive cleavage to the corresponding *cis*- and *trans*-2-substituted cyclohexylamines.

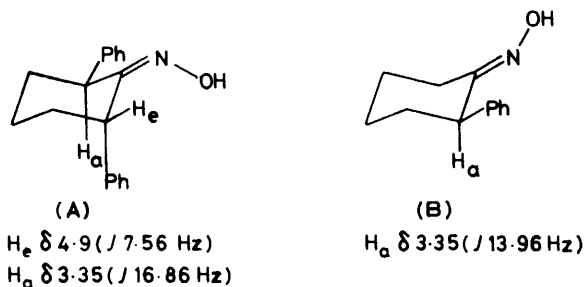
Conformation (c) for the *syn*-hydrazones is in agreement with their  $^1\text{H}$  n.m.r. spectra. Compounds (3) and

<sup>5</sup> F. Johnson, *Chem. Rev.*, 1968, **68**, 375.

<sup>6</sup> F. Johnson and D. T. Dix, *J. Amer. Chem. Soc.*, 1971, **93**, 5931.

(5) show a triplet [ $\delta$  4.1 ( $J$  8 Hz) and  $\delta$  4.0 ( $J$  8 Hz), respectively], corresponding to the equatorially oriented benzylic proton, whereas compound (10) exhibits a triplet [ $\delta$  3.7 ( $J$  14 Hz)] typical of the axial benzylic proton.

The benzylic proton signal of compound (8) is partially overlapped by that of the methoxy-group, but (8) must

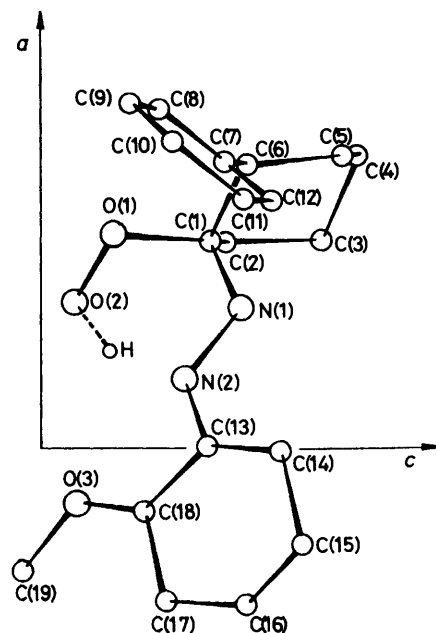


have the same conformation as (10). These spectroscopic data agree with those for *trans*-2,6-diphenylcyclohexanone oxime<sup>6</sup> (A) and 2-phenylcyclohexanone oxime<sup>6</sup> (B).

Compounds (4) and (6) show a doublet [ $\delta$  1.15 ( $J$  7.5 Hz)] corresponding to the axial methyl group, whereas in compounds (9) and (11) the methyl group [doublet,  $\delta$  1.20 ( $J$  6 Hz)] is equatorially oriented.

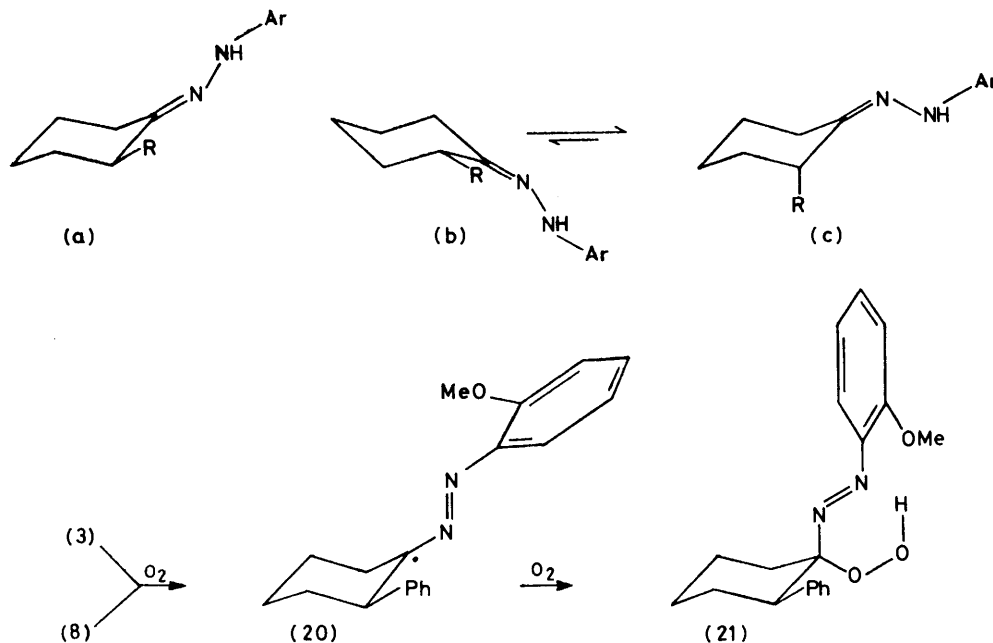
Phenylhydrazones are known to undergo autoxidation to the corresponding phenylazo-hydroperoxides.<sup>7,8</sup> During the present work we observed that both *syn*- and

by X-ray analysis (see Figure). The O(1)–O(2) bond length [1.48(1) Å] agrees with that found in other peroxy-



Projection of the molecule (21) along the  $b$  axis

compounds. The O(2)–N(2) distance [2.66(1) Å] suggests an intramolecular hydrogen bond involving the hydrogen atom of the hydroperoxy-group. In fact the electron-



SCHEME 3

*anti*-hydrazones easily underwent autoxidation, furnishing the same products. One of these, 1-hydroperoxy-1-(*o*-methoxyphenylazo)-2-phenylcyclohexane (21), is fairly stable and we were able to determine its structure

density difference map clearly showed a peak attributable to the hydrogen atom of the bent  $O-H \cdots N$  bridge. The cyclohexane ring has a nearly regular

<sup>7</sup> R. Crigee and G. Lohaus, *Chem. Ber.*, 1951, **84**, 219.

<sup>8</sup> F. Minisci, *Gazzetta*, 1959, **89**, 626; G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, 1963, **85**, 3624.

chair conformation, the plane of the C(7)–C(12) phenyl group (planar within 0.006 Å) intersecting the aliphatic ring along the C(3)–C(6) direction (see Figure). The latter atoms are displaced from the phenyl least-squares plane by  $-0.416$  and  $0.003$  Å, respectively. The aromatic ring bonded to N(2) is planar within 0.02 Å and the methyl carbon atom is slightly displaced (0.218 Å) from this plane. Furthermore this phenyl group is rotated *ca.* 25° about the N(2)–C(13) bond to alleviate steric repulsion. This, in turn, hinders delocalization of

N, 13.05. C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O requires C, 72.2; H, 7.45; N, 12.95%.

*Reactions of the Arylazocyclohexenes (1) and (7) with Grignard Reagents.*—The reactions were carried out with the Grignard reagents (PhMgBr or MeMgI) in molar ratios of 2.5 : 1 with respect to the azo-derivative (1) and 4 : 1 with respect to (7). With the aromatic Grignard reagent the reactions were complete within 3 h; with the aliphatic reagent within 2 h. The mixtures were hydrolysed with aqueous 20% ammonium chloride. The organic layers were washed with water until neutral, dried, and evaporated.

TABLE I  
Physical and analytical data for hydrazone derivatives

Compd.	M.p. (°C)	Formula	Found (%)			Required (%)		
			C	H	N	C	H	N
(3)	93–94.5 <sup>a</sup>	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O	77.4	7.55	9.4	77.5	7.55	9.5
(4)	75–77 <sup>b</sup>	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O	72.0	8.8	11.9	72.4	8.7	12.05
(5)	61–62 <sup>c</sup>	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub>	81.5	7.85	10.45	81.8	7.65	10.6
(8)	92–94 <sup>d</sup>	C <sub>18</sub> H <sub>22</sub> N <sub>2</sub> O	77.2	7.35	9.75	77.5	7.55	9.5
(9)	68–71 <sup>b</sup>	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O	72.4	8.4	12.1	72.4	8.7	12.05
(10)	47–48 <sup>d</sup>	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub>	81.4	7.65	10.65	81.8	7.65	10.6
(11)	41–43 <sup>e</sup>	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub>	77.1	9.05	13.9	77.2	8.95	13.85

<sup>a</sup> From ethanol. <sup>b</sup> Washed with light petroleum and recrystallized from ethanol. <sup>c</sup> Freed from biphenyl by washing with light petroleum and recrystallized from ethanol. <sup>d</sup> Washed with methanol and recrystallized from ethanol. <sup>e</sup> Washed with light petroleum.

electrons between the phenyl and the azo-group. The latter, in the expected *trans*-configuration, is characterized by an N–N bond length of 1.28(1) Å.

Autoxidation of compounds (3) and (8) proceeds by the known mechanism<sup>7</sup> to form the hydroperoxide (21), by attack of oxygen on the radical (20) from the most sterically favoured side of the molecule (Scheme 3).

#### EXPERIMENTAL

Analytical t.l.c. plates were coated with silica gel G (Merck). Analytical g.l.c. was carried out with a Perkin-Elmer F 11 flame ionization chromatograph with an 8 ft steel column (1/8 in diam.) containing Carbowax 20 M–KOH on Chromosorb W (nitrogen flow rate 20 ml min<sup>-1</sup>).

<sup>1</sup>H N.m.r. spectra were recorded for solutions in deuteriochloroform (with tetramethylsilane as internal standard), with a JEOL JNM 60 HL spectrometer. U.v. spectra were determined for solutions in 95% ethanol with a Perkin-Elmer 124 spectrophotometer.

Catalytic hydrogenations were carried out in a Parr apparatus at room temperature and at low pressure. Grignard reactions were carried out in anhydrous ether with stirring, at room temperature, under dry oxygen-free nitrogen. Solvents, including water, and aqueous solutions were de-aerated to prevent formation of hydroperoxides. Solutions were dried over sodium sulphate. Solvents were removed under reduced pressure below 25 °C. Light petroleum refers to the fraction of b.p. 40–70 °C.

All crude hydrazone derivatives were stored at *ca.* –20 °C; their preliminary purification was carried out at the same temperature.

*1-(o-Methoxyphenylazo)cyclohexene (1).*—This compound was prepared<sup>3</sup> from *o*-methoxyphenylhydrazine and 2-chlorocyclohexanone. When stored in a refrigerator, the viscous oil obtained after chromatography on alumina (Merck) (elution with light petroleum) gave yellow-orange crystals (1) (75%), m.p. 48 °C (Found: C, 72.0; H, 7.55;

<sup>3</sup> A. H. Kelly, D. H. McLeod, and J. Parrick, *Canad. J. Chem.*, 1965, **43**, 296.

ated. Physical and analytical data for the products (3)–(6) are reported in Table 1. As the oily compound (6) underwent autoxidation and decomposed rapidly, no satisfactory analytical figures were obtained. It was identified from the nature of its cleavage products.

*The Hydrazones (8)–(11).*—These products were obtained by reactions of 2-phenyl- and 2-methyl-cyclohexanone with *o*-methoxyphenyl- and phenyl-hydrazine, carried out in anhydrous ether, in the presence of anhydrous sodium sulphate, at room temperature, with stirring for 2–3 h. Sodium sulphate was filtered off, and the solvent removed. Physical and analytical data are reported in Table 1. Compound (10) is known,<sup>9</sup> but the literature data are sparse.

TABLE 2

G.l.c. data for isomeric 2-substituted cyclohexylamines

Substituent	Column temp. (°C)	<i>t<sub>R</sub></i> /min		Ref.
		<i>cis</i>	<i>trans</i>	
Ph	190	14.0	12.0	<i>a</i>
Me	85	20.5	18.5	<i>b</i>

<sup>a</sup> T. Masamune, M. Ohno, M. Koshi, S. Ohuchi, and T. Iwadare, *J. Org. Chem.*, 1964, **29**, 1419. <sup>b</sup> H. Booth, G. C. Gidley, and N. C. Franklin, *Tetrahedron*, 1967, **23**, 2421.

*Reductive Cleavage of the Hydrazones (3)–(6) and (8)–(11).*—Raney nickel T-1 (1 g)<sup>4</sup> and aqueous 20% sodium hydroxide (0.3 ml) were added to a solution of the hydrazone derivative (10 mmol) in 95% ethanol (100 ml). Hydrogenation was complete within 6 h. After removal of the catalyst, the solution was evaporated under reduced pressure at 40–50 °C and the residue was dissolved in ether. The solution was washed with water, dried, and concentrated. The products were identified by g.l.c. (comparison with authentic samples). Compounds (3), (4), (8), and (9), and compounds (5), (6), (10), and (11) gave *o*-anisidine and aniline, respectively, together with the 2-substituted cyclohexylamines (*cis* : *trans* ratio 60 : 40). G.l.c. data for the *cis*- and *trans*-cyclohexylamines are reported in Table 2.

*Reduction–Oxidation of the Hydrazones (3)–(6) and (8)–(11) to the Azo-compounds (12)–(19).*—To a solution of the

appropriate hydrazone (3)—(6) or (8)—(11) (10 mmol) in methanol (100 ml), a solution of sodium borohydride (0.4 g) in water (2 ml) was added, with stirring, at room temperature. Stirring was continued until the reduction was complete (t.l.c.) (ca. 6 h). The mixture was treated with water and extracted with ether. The extract was washed until neutral, dried, and treated with mercury(II) oxide (4 g) with

Cell parameters were determined from Weissenberg and precession photographs taken with Cu- $K_{\alpha}$  radiation.

*Intensity measurements.* The X-ray intensity data were collected by the equi-inclination Weissenberg method (Cu- $K_{\alpha}$  radiation) and estimated by visual comparison with a calibrated scale. Levels  $hk0$ —7 and  $0kl$ —1 were recorded by the multiple-film technique. Since the compound is

TABLE 3  
Physical and analytical data for azo-compounds

Compd.	M.p. (°C)	Formula	Found (%)			Required (%)		
			C	H	N	C	H	N
(12)	132—133 <sup>a</sup>	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O	77.2	7.55	9.7	77.5	7.55	9.5
(13)	(Oil)	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O	72.5	8.85	11.9	72.4	8.7	12.05
(14)	34—35 <sup>b</sup>	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub>	81.8	7.2	10.7	81.8	7.65	10.6
(15)	(Oil)	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub>	76.85	9.2	13.9	77.2	8.95	13.85
(16)	78—79 <sup>a</sup>	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O	77.5	7.5	9.6	77.5	7.55	9.5
(17)	(Oil)	C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O	72.6	8.75	12.3	72.4	8.7	12.05
(18)	48—50 <sup>b</sup>	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub>	81.8	7.85	10.5	81.8	7.65	10.6
(19)	(Oil)	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub>	77.3	9.15	13.8	77.2	8.95	13.85

<sup>a</sup> From light petroleum. <sup>b</sup> From ethanol.

stirring. Stirring was continued for 1 h. The products (12)—(19) were separated and purified by column chromatography (Merck silica gel 60, 70—230 mesh; light petroleum—benzene, 2:1). U.v. spectra of all the azo-compounds show characteristic absorption in the region 400—415 nm. Physical and analytical data of the products (12)—(19) are reported in Table 3.

*Reductive Cleavage of the Azo-compounds (12)—(19).*—The reduction was carried out under the conditions already described for the hydrazones. The products were identified by g.l.c. (comparison with authentic samples). Compounds (12)—(15) gave *cis*-2-substituted cyclohexylamines,

stable only at low temperature, all the X-ray data were collected at about -30 °C with the crystal enclosed in a thin-walled capillary tube. The swiftness of recording did not allow us to obtain an 'ideal' set of data; however the data were sufficiently good for performing the crystal structure analysis using 1 170 independent reflections.

*Structure determination and refinement.* The structure

TABLE 4

Reduction-oxidation of arylhydrazones

Arylhydrazones	Azo-compounds		Ratio (%) ( <i>cis</i> : <i>trans</i> )
	<i>cis</i>	<i>trans</i>	
(3)	(12)	(16)	88 : 12
(4)	(13)	(17)	93 : 7
(5)	(14)	(18)	85 : 15
(6)	(15)	(19)	90 : 10
(8)	(12)	(16)	39 : 61
(9)	(13)	(17)	62 : 38
(10)	(14)	(18)	40 : 60
(11)	(15)	(19)	66 : 34

whereas from (16)—(19) the *trans*-isomers were obtained, together with the corresponding arylamine.

The mixtures of azo-compounds obtained from the hydrazones were subjected to reductive cleavage. The ratios of the *cis*- and *trans*-2-substituted cyclohexylamines (g.l.c. analysis) correspond to those (reported in Table 4) of the azo-compounds in the starting mixtures.

*1-Hydroperoxy-1-(o-methoxyphenylazo)-2-phenylcyclohexane (21).*—Autoxidation of compounds (3) and (8) occurred both in ether and in light petroleum and gave the *hydroperoxide* (21) as deep yellow crystals, m.p. 28 °C (decomp.) (from ether, with cooling) (Found: C, 69.8; H, 6.8; N, 8.2. C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> requires C, 69.9; H, 6.8; N, 8.6%).

*Crystallography.*—*Crystal data:* C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>,  $M = 326.3$ . Monoclinic,  $a = 11.13(2)$ ,  $b = 14.04(3)$ ,  $c = 11.18(2)$  Å,  $\beta = 90.6(5)^\circ$ ,  $U = 1747.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.24$  g cm<sup>-3</sup>. Cu- $K_{\alpha}$  radiation,  $\lambda = 1.5418$  Å;  $\mu(\text{Cu-}K_{\alpha}) = 6.92$  cm<sup>-1</sup>. Space group  $P2_1/c$  ( $C_2^5$ ).

<sup>10</sup> G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

TABLE 5

Bond lengths (Å) and angles (°), with their estimated standard deviations in parentheses

O(1)—O(2)	1.48(1)	C(7)—C(8)	1.38(1)
N(1)—N(2)	1.28(1)	C(7)—C(12)	1.40(1)
O(1)—C(1)	1.42(1)	C(8)—C(9)	1.39(1)
O(3)—C(18)	1.36(1)	C(9)—C(10)	1.39(1)
N(1)—C(1)	1.47(1)	C(10)—C(11)	1.38(1)
N(2)—C(13)	1.41(1)	C(11)—C(12)	1.39(1)
C(1)—C(2)	1.54(1)	C(13)—C(14)	1.38(1)
C(2)—C(3)	1.53(1)	C(13)—C(18)	1.42(1)
C(3)—C(4)	1.56(1)	C(14)—C(15)	1.38(1)
C(4)—C(5)	1.53(1)	C(15)—C(16)	1.41(1)
C(5)—C(6)	1.54(1)	C(16)—C(17)	1.38(1)
C(6)—C(7)	1.54(1)	C(17)—C(18)	1.38(1)
O(2)—O(1)—C(1)	110.7(6)	C(6)—C(7)—C(12)	121.4(7)
C(18)—O(3)—C(19)	117.0(7)	C(8)—C(7)—C(12)	118.7(8)
N(2)—N(1)—C(1)	120.0(6)	C(7)—C(8)—C(9)	121.4(9)
N(1)—N(2)—C(13)	117.7(7)	C(8)—C(9)—C(10)	118.9(4)
O(1)—C(1)—N(1)	113.9(7)	C(9)—C(10)—C(11)	120.8(9)
N(1)—C(1)—C(2)	108.7(7)	C(10)—C(11)—C(12)	119.9(8)
O(1)—C(1)—C(6)	102.3(6)	N(2)—C(13)—C(14)	124.7(8)
C(2)—C(1)—C(6)	110.5(7)	N(2)—C(13)—C(18)	115.4(7)
C(1)—C(2)—C(3)	112.9(3)	C(14)—C(13)—C(18)	119.8(8)
C(2)—C(3)—C(4)	109.5(8)	C(13)—C(14)—C(15)	120.0(9)
C(3)—C(4)—C(5)	119.6(8)	C(14)—C(15)—C(16)	120.7(8)
C(4)—C(5)—C(6)	110.8(7)	C(15)—C(16)—C(17)	119.3(9)
C(1)—C(6)—C(5)	111.1(7)	C(16)—C(17)—C(18)	120.5(8)
C(1)—C(6)—C(7)	111.7(7)	O(3)—C(18)—C(13)	115.0(7)
C(5)—C(6)—C(7)	113.3(6)	O(3)—C(18)—C(17)	125.2(8)
C(6)—C(7)—C(8)	119.9(8)		

was determined by direct methods by using the MULTAN program<sup>10</sup> and refined by the block-diagonal matrix least-squares technique. After anisotropic refinement the conventional  $R$  factor was 0.13. At this stage a three-dimensional Fourier synthesis was undertaken to locate the hydrogen atoms. Estimated positions for these atoms were all in regions of positive electron density. All the hydrogen atoms were included at calculated positions with the temperature factors set at 5 Å<sup>2</sup>. Final anisotropic least-squares refinement reduced  $R$  to 0.10. Bond lengths and angles

with standard deviations are listed in Table 5. Some significant torsion angles are reported in Table 6.

TABLE 6

Some significant torsion angles (°)

C(1)-N(1)-N(2)-C(13)	179.0
C(1)-O(1)-O(2)-H	119.1
C(3)-C(1)-C(12)-C(6)	53.8
C(1)-C(2)-C(3)-C(4)	123.0
C(2)-C(3)-C(4)-C(5)	59.2
C(3)-C(4)-C(5)-C(6)	120.0
C(1)-C(5)-C(6)-C(4)	57.0
C(2)-C(1)-C(6)-C(5)	127.1
N(1)-N(2)-C(13)-C(18)	157.8
C(13)-C(18)-O(3)-C(19)	172.0

The numbering scheme for the atoms is shown in the Figure. Observed and calculated structure factors, final atomic parameters, and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22022 (6 pp.).\*

Atomic scattering factors were calculated according to ref. 11.

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\* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1976, Index issue.

<sup>11</sup> F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.