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REACTIONS OF CONJUGATED ARYLAZOCYCLOALKENES WITH GRIGNARD REAGENTS—4[3]

PARALLEL AND ANTIPARALLEL ATTACKS OF GRIGNARD HYDROCARBON MOIETY ON SOME ARYLAZOCYCLOALKENES

SILVANO BOZZINI, SERGIO GRATTON, ADRIANA LISINI, GIORGIO PELLIZER and AMERIGO RISALITI*
Istituto di Chimica, Università, 34127 Trieste, Italy

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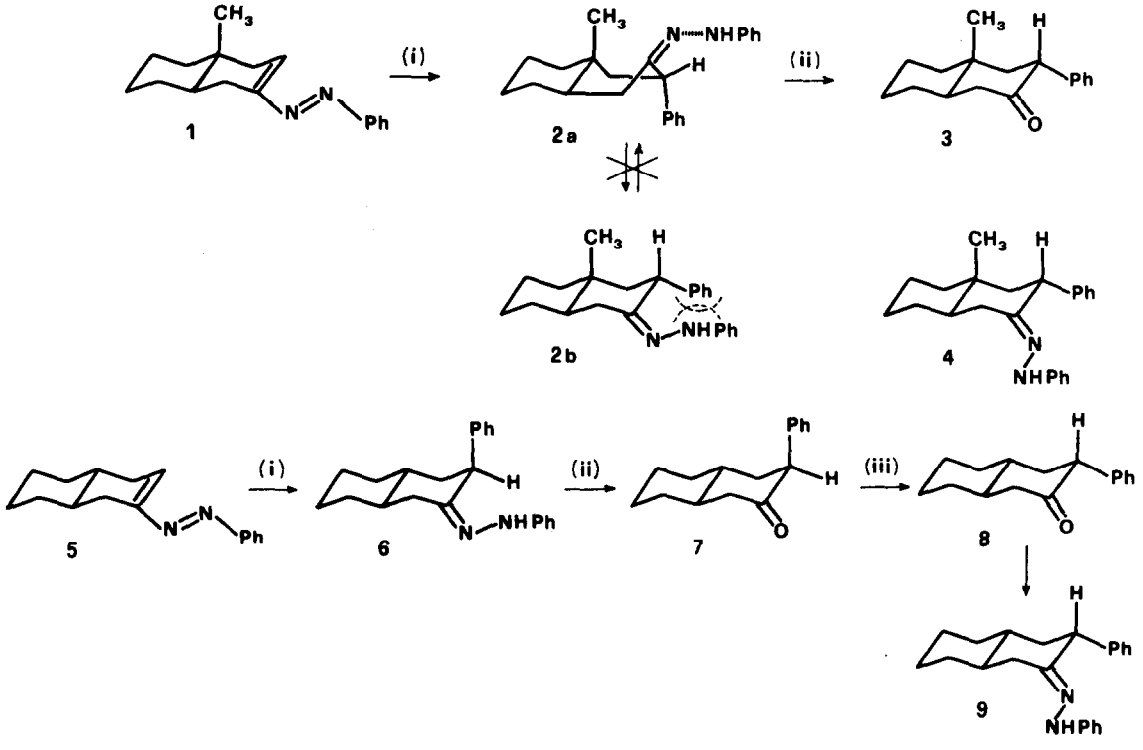
Abstract—Conjugated phenylazocycloalkenes sterically hindered towards the antiparallel attack react with PhMgBr via parallel attack, to give *syn*-phenylhydrazones. When such a sterical hindrance is absent in the azoalkenes, the reaction occurs via antiparallel attack even when the arylmagnesium bromide bears a particularly hindering aryl group. The conformation of the *syn*-phenylhydrazones obtained by the above reactions and those of the corresponding ketones are discussed with the aid of the benzylic proton NMR analysis.

We have shown that the reaction of conjugated phenylazocyclohexenes with Grignard reagents leads to 2-aryl- and 2-alkyl-cyclohexanone phenylhydrazones in *syn*-configuration.[1-3] Their preferred conformation is a chair with the C-2 substituent axially oriented, in agreement with the proposed reaction mechanism[1] and with the antiparallel attack of the reactant.[2]

Our purposes in this work are to investigate: (i) Grignard reactions with conjugated arylazocycloalkenes sterically hindered towards the antiparallel attack; (ii) reactions of non-sterically hindered arylazocycloalkenes with arylamagnesium halides bearing particularly bulky aryl groups.

As to point (i), we have considered 2 - phenylazo - 4a - methyl - *trans* - Δ^2 - octalin **1** where the angular methyl group prevents the antiparallel attack. Reacting compound **1** with PhMgBr, 3 - phenyl - 4a - methyl - *trans* - decalin - 2 - one phenylhydrazone **2** was obtained in high yield (Scheme 1). Non epimerizing hydrolysis[2,4] of compound **2** led to 3 - phenyl - 4a - methyl - *trans* - decalin -



Scheme 1. Reagents: (i) PhMgBr; (ii) $NaJO_4$ (pH 7); (iii) pyrrolidine (dilute MeOH).

2 - one **3** with the C-3 phenyl group in an equatorial position.

The structure of compound **3** is inferred from its stability under equilibrating conditions and from the ^{1}H NMR spectrum where the resonances of the C-3 benzylic proton appear as a doublet of doublets. Approximate estimates of coupling constants obtained through rough first order approximation are $J_{a,a} \sim 12$ Hz and $J_{a,e} \sim 7$ Hz.

These results indicate a parallel attack of the reactant at C-3 of compound **1**. Regarding the configuration of **2** it has not been possible to get information from the comparison with the *anti*-phenylhydrazone **4** synthetized from ketone **3** as compound **4** rapidly autoxidized to the corresponding phenylazohydroperoxide.[1] Nevertheless it turned out in many other cases that *anti*-phenylhydrazones from equatorially α-substituted alkanones present very similar ^{1}H NMR patterns regarding benzylic protons. For instance the following values are significant:

	δ ($CDCl_3$)	W_H^* (Hz)
α-3-phenyl-*trans*-decalin-2-one **8**	3.8–3.4	17
α-3-phenyl-*trans*-decalin-2-one *anti* phenylhydrazone **9**	3.7–3.3	20
cis-2-phenyl-4-*t*-butyl-cyclohexanone[2]	3.75–3.45	17.5
cis-2-phenyl-4-*t*-butyl-cyclohexanone *anti*-phenylhydrazone **23**	3.6–3.3	17

W_H^* distance between external peaks.

The W_H value found for the benzylic proton of **2** (δ 4.1, W_H 10 Hz) is remarkably smaller than those reported above and therefore it is not consistent either with the *anti* configuration **4** or with the *syn* one in chair conformation **2b**, whilst it is consistent with the *syn* configuration in a twist-boat conformation **2a**. In addition, the benzylic proton multiplet appears as a sort of double doublet in which the spacing between the external peak and the nearer inner peak is about 2 Hz. We noted by spectra simulation that this multiplet pattern is consistent only with vicinal coupling constants of 8–10 Hz and 2–0 Hz and that the spacing between the external peak and the nearer inner peak is an upper limit to the smaller coupling constant. Using the Karplus equation,[5] the values found are in accordance with dihedral angles around 30° and 90° respectively.

The conformational preference of **2a** over **2b** indicates that the energy related with Ph/NH-Ph $A^{1,3}$ allylic strain[6,7] in **2b**, is stronger than that related with the twist-boat **2a** in which the Ph group is *quasi* axially oriented but $A^{1,3}$ strains are absent. Furthermore, the formation of the *syn*-compound **2a** indicates that the reaction mechanism of conjugated phenylazocycloalkenes with Grignard reagents always results in a 1,4-conjugated addition[2] whatever the attack of the reactant is.

As expected, compound **5** which is not sterically hindered to the antiparallel attack, on reaction with PhMgBr gives the *syn* phenylhydrazone **6** (the benzylic proton shows a pseudo triplet, δ 4.15, W_H 10 Hz) (Scheme 1). Non-epimerizing hydrolysis of **6** gives the ketone **7** (pseudo triplet, δ 3.9–3.65, W_H 9 Hz for the benzylic proton) which can be converted easily into the thermodynamically more stable isomer **8** (pseudo quartet, δ 3.9–3.4, W_H^* 17 Hz, for the benzylic proton).

Antiparallel attacks can also be hindered by hydrocarbon groups in vicinal position with respect to the reaction centre.[8] For instance, the Δ^1 enamines derived from 3-phenyl- and 3 - *t* - butyl - cyclohexanone do not undergo antiparallel attack owing to the *gauche* interaction with the entering group and react via parallel attack.[9]

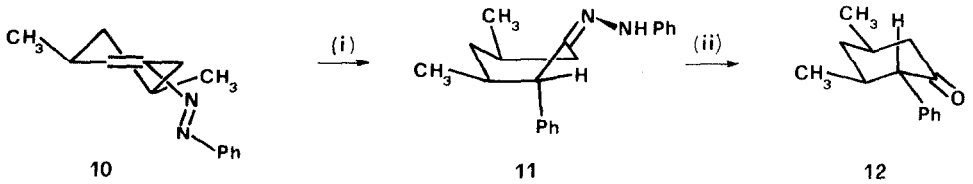
The same stereochemistry is found in the reaction of PhMgBr with 1-phenylazo-3,5-dimethyl-cyclohexene **10**, where the ring inversion is precluded by the strong 1,3-interaction of the methyls in the diaxial conformer (Scheme 2). The attack of Grignard phenyl group at the C-2 position of **10** gives the *syn*-hydrazone **11**. In this compound the benzylic proton resonances overlap with those of another cycloaliphatic ring proton (probably the one at C-3). The parallel attack is proved by the controlled hydrolysis of **11** which gives directly the more stable all *cis* isomer **12**, where the benzylic proton resonances appear as a doublet (δ 3.15, $^3J_{HH}$ 11.5 Hz).

In accordance with the above conclusions regarding compound **2**, the chair conformation with the phenyl in an equatorial position can also be excluded for compound **11** due to allylic strain.

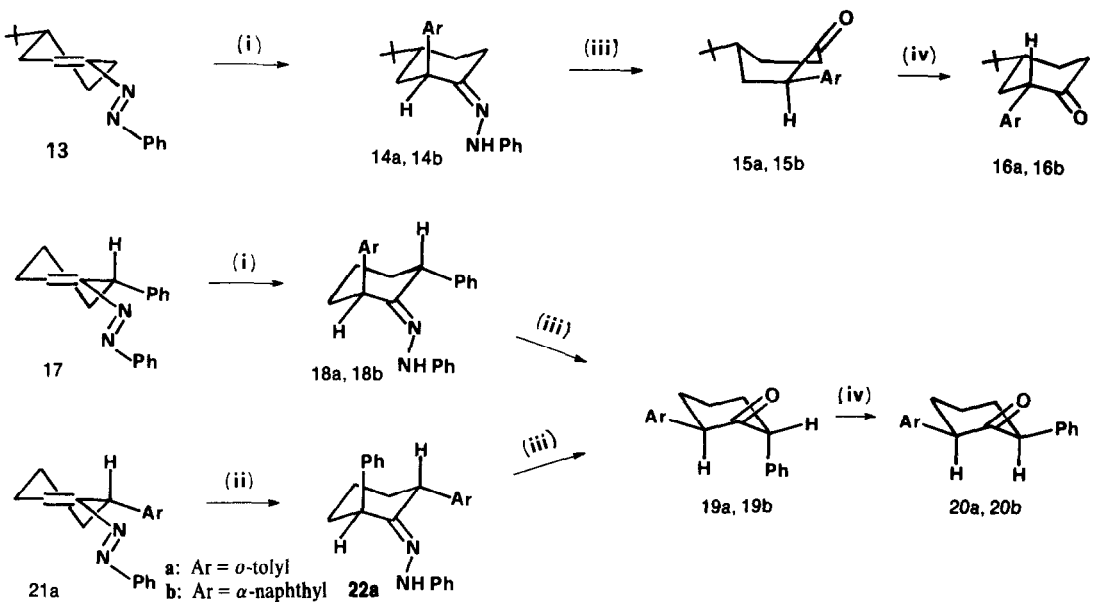
As to point (ii) we have found that *o*-tolyl- and α - naphthyl - magnesium bromide react easily by antiparallel attack with 4 - *t* - butyl - 1 - phenylazocyclohexene **13**, differently from what we suggested in a preceding paper.[2]

In fact, from the above reactions, phenylhydrazones **14a** and **14b** were obtained and their structure was deduced from their controlled hydrolysis leading to *trans* ketones **15a** and **15b** which were easily converted into the *cis* isomers **16a** and **16b** by equilibration (Scheme 3). Phenylhydrazones **14a** and **14b** exhibit in their ^{1}H NMR spectra a signal at δ 4.25–4.0 (W_H 10 Hz) and δ 5.0–4.75 (W_H 9 Hz) respectively, attributable to equatorial benzylic protons. This would be in agreement with chair conformations; however, from inspection of molecular models, such conformations have to be, in our opinion, somewhat flattened owing to the strong steric hindrance of the axial bulky Ar groups.

In the *trans* ketones **15a** and **15b** the C-2 proton resonances appear as pseudo triplets with external peaks 15.5 Hz and 13 Hz apart, respectively. These values rule out for such protons an equatorial orientation in chair conformations and would be consistent with twist-boat conformations in which steric interactions of Ar groups are somewhat relieved. In *cis* ketones **16a**[2] and **16b**[2] the



Scheme 2. Reagents: (i) PhMgBr; (ii) $NaJO_4$ (pH 7).



Scheme 3. Reagents: (i) ArMgBr; (ii) PhMgBr; (iii) $NaJO_4$ (pH 7); (iv) pyrrolidine (dilute MeOH).

C-2 proton resonances give rise to pseudo quartets with distances between external peaks of 17.5 Hz† and 16 Hz respectively, in agreement with the expected chair conformation.

In order to verify the reactivity of sterically hindered Grignard reagents with other phenylazocyclohexenes, we have taken into consideration the reactions of 6 - phenyl - 1 - phenylazo - cyclohexene[3] **17** with *o*-tolyl- and α-naphthyl-magnesium bromide. Moreover, these reactions allowed us to obtain 2,6-diaryl-derivatives having benzylic protons in 2 and 6 positions, the resonances of which could give better structural information.

From the reaction of α-naphthylmagnesium bromide with **17**, *trans* - 2 - α - naphthyl - 6 - phenyl - cyclohexanon - *syn* - phenylhydrazone **18b** was formed, the ^{1}H NMR spectrum of which shows distinct signals for benzylic protons, that is a multiplet at δ 4.8–4.5 (W_H^* 12 Hz) for the C-2 proton and another multiplet at δ 4.25–3.85 (W_H^* 16.5 Hz) for the C-6 proton. These values are in poor agreement with a rigid chair conformation and taking into account that $A^{1,3}$ allylic strain between α-naphthyl and NH–Ph groups has to be avoided, it is likely that they reflect a fairly flattened chair conformation, chiefly on α-naphthyl side. The controlled hydrolysis of **18b** leads to the *trans* ketone **19b**, for which the chair conformation with α-naphthyl and phenyl groups in equatorial and axial orientation respectively predominates. This can be inferred from the signals at δ 4.6–4.25 (W_H^* 15 Hz) and at δ 4.2–3.8 (W_H 9.5 Hz) for the C-2 and C-6 proton, respectively.

The reaction of **17** with *o*-tolylmagnesium bromide furnishes phenylhydrazone **18a**. Unfortunately in its ^{1}H NMR spectrum the C-2 and C-6 proton signals overlap.

Exchanging the same substituents in C-2 and C-6 positions (compound **22a**), distinct benzylic proton signals are observed: δ 4.3–4.05, W_H 10 Hz and δ 4.05–3.65, W_H^* 17.5 Hz for the C-2 and C-6 proton, respectively.

†The 12.8 Hz value previously reported (see Ref. 2) is due to a misprint.

Under the usual conditions, both **18a** and **22a** are converted into the *trans* ketone **19a**. The *trans* ketones **19a** and **19b** by equilibration furnished the corresponding *cis* isomers **20a** and **20b**.

The reaction mechanism of conjugated arylazocyclohexene with Grignard compounds requires that the C=C–N=N system lies in S-*cis* conformation.[2] Therefore, it seemed interesting to examine reactions of conjugated arylazocycloalkenes in which such a system is forced in an S-*trans* conformation. To this end we synthetized 1 - phenylazo - 2 - methyl - cyclohexene in which, to avoid CH_3/=N–Ph allylic interaction, the S-*trans* resulted in the more stable conformation. The fact that this azocompound was recovered unchanged from reaction with many Grignard reagents under various conditions, confirms once again the reported machanism.

EXPERIMENTAL

^{1}H NMR spectra were recorded with a JEOL JNM 60 HL spectrometer ($SiMe_4$ as internal standard). The computer program for simulation of spectra was set up in our laboratories. Calculations were performed on a CDC CYBER 170 computer. IR spectra were recorded by a Perkin–Elmer 297 spectrophotometer and UV spectra by a Perkin–Elmer 124 spectrophotometer for solns in 95% EtOH. Analytical tlc plates were coated with silica gel G (Merck). Phenylazocycloalkenes were purified by column chromatography on alumina (Merck) (elution with light petroleum, b.p. 40–70°). Cycloalkanones were purified by column chromatography on extra pure. silica gel (Merck 70–230 mesh ASTM, elution with benzene).

2-o-Tolyl-cyclohexanone-syn-*phenylhydrazone.* This compound was obtained from 1-phenylazocyclohexene and *o*-tolylmagnesium bromide using the same method as described for 2 - phenyl - cyclohexanone - *syn* - phenylhydrazone,[1] white crystals, m.p. 66–67° (from ethanol). (Found: C, 81.7; H, 8.1; N, 9.75. $C_{19}H_{22}N_2$ requires C, 81.95; H, 7.95; N, 10.05%); δ ($CDCl_3$) 7.5–6.4 (10 H, m, Ar-H and NH), 3.8–3.4 (1H, m, W_H^* 13.5 Hz, CHAr), 3.05–0.9 (8H, m, aliphatic ring H), 2.1 (3H, s, ArMe).

2-o-Tolyl-cyclohexanone. This ketone was prepared from 2 - *o* - tolyl - cyclohexanone - *syn* - phenylhydrazone by hydrolysis with HNO_3 10%.[2] White crystals, m.p. 58–59° (from light petroleum 30–50°). (Found: C, 83.1; H, 8.75. $C_{13}H_{16}O$ requires C,

Table 1. Physical, analytical, and spectral data of phenylazocycloalkenes (1, 5, 10, 21a)

Compound	M.p. (°C)	Formula	Analysis (%) Found C	Found H	Found N	Required C	Required H	Required N	λ_{max} [a]/nm	δ ($CDCl_3$)
1	44-45 (light petroleum 30-50°)	$C_{17}H_{22}N_2$	80.4	8.85	10.9	80.25	8.7	11.0	427	7.95-7.25(5H,m,Ar-H),7.0-6.75 (1H,m,W_H 9 Hz,vinyl H), 2.8-1.1(13H,m,aliphatic ring H),0.85(3H,s,Me)
5	69.5-70.5 (ethanol)	$C_{16}H_{20}N_2$	80.1	8.35	11.8	79.95	8.4	11.65	427	7.9-7.2(5H,m,Ar-H),7.0-6.6 (1H,m,W_H 6 Hz,vinyl H), 3.0-0.6(14H,m,aliphatic ring H)
10	oil	$C_{14}H_{18}N_2$	78.3	8.6	12.9	78.45	8.45	13.05	427	7.95-7.2(5H,m,Ar-H),6.9-6.7 (1H,m,W_H 5 Hz,vinyl H) 2.9-1.4(6H,m,aliphatic ring H),1.15(3H,d,J 6.5 Hz,Me), 1.05(3H,d,J 6.0 Hz,Me)
21a	47-48 (light petroleum 30-50°)	$C_{19}H_{20}N_2$	82.3	7.25	9.9	82.55	7.3	10.15	434	7.7-6.9(10H,m,Ar-H and vinyl H), 4.55-4.3(1H,m,W_H 8.5 Hz, CH-Ar),2.5(3H,s,Ar-Me),2.3-1.4(6H,m,aliphatic ring H)

[a] N=N band (n-π*)

Table 2. Physical, analytical, and spectral data of cycloalkanone phenylhydrazones (2, 6, 9, 11, 14a, 14b, 18a, 18b, 22a, 23)

Compound	M.p. (°C)	Formula	Analysis (%) Found C	Found H	Found N	Required C	Required H	Required N	δ ($CDCl_3$)
2	110-111 (light petroleum)	$C_{23}H_{28}N_2$	82.9	8.7	8.45	83.1	8.5	8.45	7.4-6.45(11H,m,Ar-H and NH),4.3-4.0 (1H,m,W_H 9 Hz,CHPh),2.75-0.9(13H,m, aliphatic ring H), 0.5(3H,s,Me)
6	87-89 (light petroleum)	$C_{22}H_{26}N_2$	82.7	8.2	8.55	82.95	8.25	8.8	7.6-6.6(11H,m,Ar-H and NH),4.35-4.05 (1H,m,W_H 10 Hz,CHPh), 3.25-0.6(14H, m,aliphatic ring H)
9	126-128 (light petroleum)	$C_{22}H_{26}N_2$	82.85	8.3	8.6	82.95	8.25	8.8	7.6-6.5(11H,m,Ar-H and NH),3.7-3.3 (1H,m,W_H^* 20Hz,CHPh),3.0-0.9(14H,m, aliphatic ring H)
11	94-96 (light petroleum)	$C_{20}H_{24}N_2$	82.05	8.45	9.65	82.15	8.25	9.6	7.6-6.6(11H,m,Ar-H and NH),3.25-1.6 (7H,m,aliphatic ring H and CHPh), 1.02(3H,d,J 6 Hz,Me),0.85(3H,d, J 6.75 Hz, Me)
14a	107-108 (ethanol)	$C_{23}H_{30}N_2$	82.5	9.0	8.3	82.6	9.05	8.35	7.3-6.4(10H,m,Ar-H and NH), 4.25-4.0 (1H,m,W_H 10 Hz,CHAr),2.9-1.1(7H,m, aliphatic ring H),2.4(3H,s,ArMe),0.8 (9H,s,CMe_3)
14b	145-147 (ethanol)	$C_{26}H_{30}N_2$	84.4	8.05	7.5	84.3	8.15	7.55	8.35-6.25(13H,m,Ar-H and NH),5.0-4.75 (1H,m,W_H^* 9 Hz,CHAr),3.1-0.75(7H,m, aliphatic ring H),0.75(9H,s,CMe_3)
18a	98-100 (light petroleum)	$C_{25}H_{26}N_2$	84.6	7.35	8.05	84.7	7.4	7.9	7.9-6.2(15H,m,Ar-H and NH),4.2-3.85 (2H,m,W_H 16 Hz, CHPh and CHAr), 2.6-1.4(6H,m,aliphatic ring H), 2.4(3H,s,ArMe)
18b	107-109 (methanol)	$C_{28}H_{26}N_2$	86.4	6.75	7.2	86.1	6.7	7.15	8.15-5.9(18H,m,Ar-H and NH),4.8-4.5 (1H,m,W_H^* 12Hz,CHAr), 4.25-3.85(1H, m,W_H^* 16.5 Hz,CHPh),2.5-1.3(6H,m, aliphatic ring H)
22a	90-91 (light petroleum)	$C_{25}H_{26}N_2$	84.3	7.6	7.85	84.7	7.4	7.9	7.7-6.3(15H,m,Ar-H and NH),4.3-4.05 (1H,m,W_H 10 Hz,CHAr),4.05-3.65(1H,m W_H^* 17.5 Hz,CHAr),2.7-1.1(6H,m,aliphatic ring H), 2.25(3H,s,ArMe)
23	103-105 (light petroleum)	$C_{22}H_{28}N_2$	82.25	8.65	8.7	82.45	8.8	8.75	7.6-6.5(11H,m,Ar-H and NH),3.6-3.3 (1H,m,W_H^* 17 Hz,CHPh),3.1-1.2(7H,m, aliphatic ring H),0.9(9H,s,CMe_3)

W_H^* = extreme peaks distance.

Table 3. Physical, analytical, and spectral data of cycloalkanones (**3**, **7**, **8**, **12**, **15a**, **15b**, **19a**, **19b**, **20a**, **20b**)

Compound	M.p. (°C)	Formula	Analysis (%) Found C	Found H	Required C	Required H	$\nu_{max.}$ [a] /cm^{-1}	δ (CDCl$_3$)
3	79–81 (methanol)	$C_{17}H_{22}O$	84.45	9.3	84.25	9.15	1720[c]	7.4–6.9(5H,m,Ar-H),3.85–3.5(1H, m,W_H^* 19 Hz,CHPh),2.45–1.15(13H,m, aliphatic ring H), 1.2(3H,s,Me)
7	oil	$C_{16}H_{20}O$	84.25	8.9	84.15	8.85	1700[b]	7.6–7.2(5H,m,Ar-H),3.9–3.65(1H,m, W_H 9 Hz, CHPh), 2.7–0.8(14H,m, aliphatic ring H)
8	95–96 (methanol)	$C_{16}H_{20}O$	84.4	9.1	84.15	8.85	1700[c]	7.5–7.0(5H,m,Ar-H),3.85–3.4(1H,m, W_H^* 17.5 Hz, CHPh), 2.55–1.0(14H,m, aliphatic ring H)
12	oil	$C_{14}H_{18}O$	82.9	8.75	83.1	8.95	1705[b]	7.45–6.9(5H,m,Ar-H),3.25–2.9(1H,m, W_H^* 11 Hz, CHPh), 2.7–0.65(6H,m, aliphatic ring H),1.1(3H,d,J 6.0 Hz Me), 0.8(3H,d,J 6.75 Hz, Me)
15a	oil	$C_{17}H_{24}O$	83.2	9.75	83.55	9.9	1710[b]	7.15(4H,s,Ar-H),4.0–3.7(1H,m,W_H^* 15.5 Hz,CHAr),2.7–1.65(7H,m, aliphatic ring H),2.25(3H,s,ArMe), 0.95(9H,s,CMe_3)
15b	oil	$C_{20}H_{24}O$	85.3	8.45	85.65	8.65	1710[b]	8.0–7.2(7H,m,Ar-H),4.5–4.2(1H,m, W_H^* 13 Hz,CHAr),2.65–1.3(7H,m, aliphatic ring H),0.9(9H,s,CMe_3)
19a	oil	$C_{19}H_{20}O$	86.1	7.4	86.3	7.65	1710[b]	7.4–7.0(9H,m,Ar-H),4.15–3.6 (2H,m,W_H 16 Hz,CHAr),2.6–1.6 (6H,m,aliphatic ring H),1.95 (3H,s,ArMe)
19b	125–126 (ethanol)	$C_{22}H_{20}O$	87.8	6.55	87.95	6.7	1715[c]	8.0–7.0(12H,m,Ar-H),4.6–4.25 (1H,m,W_H^* 15 Hz,CHAr),4.1–3.8 (1H,m,W_H 9.5 Hz,CHPh),2.9–1.9 (6H,m,aliphatic ring H)
20a	150–151 (ethanol)	$C_{19}H_{20}O$	86.0	7.45	86.3	7.65	1710[c]	7.7–6.9(9H,m,Ar-H),4.2–3.6 (2H,m,W_H^* 27 Hz,CHAr),2.6–1.8 (6H,m,aliphatic ring H),2.2 (3H,s,ArMe)
20b	134–135 (ethanol)	$C_{22}H_{20}O$	87.9	6.6	87.95	6.7	1710[c]	8.1–6.8(12H,m,Ar-H),4.7–4.2 (1H,m,W_H^* 17 Hz,CHAr),4.2–3.7 (1H,m,W_H^* 17.5 Hz,CHPh),2.9–1.8 (6H,m,aliphatic ring H)

W_H^* = extreme peaks distance.

[a] C=O stretch. [b] Liquid film. [c] Nujol.

82.95; H, 8.55%). ν_{max} (C=O stretch, nujol) 1725 cm^{-1}. δ ($CDCl_3$) 7.4–6.9 (4H, m, Ar-H), 3.95–3.55 (1H, m, W_H^* 16.5 Hz, CHAr), 2.75–1.4 (8H, m, aliphatic ring H), 2.15 (3H, s, ArMe).

Phenylazocycloalkenes (**1**, **5**, **10**, **13**[2], **17**[3], **21a**). Compounds **1**, **5**, **10**, **21a**, were prepared from 3 - bromo - 4a - methyl - *trans* - decalin - 2 - one,[10,11] 3 - bromo - *trans* - decalin - 2 - one,[8] 2 - bromo - 3,5 - dimethyl - cyclohexanone (from *cis* 3,5-dimethyl-cyclohexanone as for 2-bromo-4-methyl-cyclohexanone[12]), and 2-bromo-6-*o*-tolyl-cyclohexanone (from 2-*o*-tolyl-cyclohexanone in the same manner as for 2-bromo-6-phenyl-cyclohexanone[3]). The crude bromo-derivative (0.02 mol) was heated in pyridine (0.02 mol) at 100° for 5 min. The mixture was cooled at room temperature, added to anhydrous THF (3 ml) and poured with stirring into a solution of phenylhydrazine (0.02 mol) in anhyd THF (20 ml) cooled at 0° (Brodka's method[13]). Stirring was continued for 3 hr. The products were obtained in 70–80% yield. Physical, analytical, and spectral data are reported in Table 1.

1-*Phenylazo*-2-*methyl-cyclohexene.* A soln of 2 - bromo - 2 - methyl - cyclohexanone[14] (0.02 mol) in ether (20 ml) was added dropwise with stirring to an ethereal soln (20 ml) of $PhNHNH_2$, (0.04 mol) at 0°. The mixture was stirred for 3 hr and the solid ($PhNHNH_2 \cdot HBr$) was filtered off. The organic layer was treated with 10% Na_2CO_3 aq (50 ml), washed until neutral, dried, and concentrated. Column chromatography of the soln afforded the azoalkene. Orange oil (Found: C, 77.7; H, 8.1; N, 14.2.$C_{13}H_{16}N_2$ requires C, 77.95; H, 8.05; N, 14.0%); δ ($CDCl_3$) 7.8–7.05 (5H, m, ArH), 2.3 (3H, s, CH_3), and 2.2–1.3 (8H, m, aliphatic ring H); λ_{max} 442 nm (N=N bond, n–π^*).

Cycloalkanone syn-*phenykhydrazones* (**2**, **6**, **11**, **14a**, **14b**, **18a**, **18b**, **22a**). The synthesis of these compounds was carried out from phenylazocycloalkenes (**1**, **5**, **10**, **13**,[2] **17**,[3] **21a**) and appropriate Grignard reagent in the same manner as reported in previous papers.[1–3] Products were obtained in almost quantitative yield. Physical, analytical, and spectral data are reported in Table 2.

α - 3 - *Phenyl* - trans - *decalin* - 2 - *one* anti - *phenylhydrazone* (**9**), *and* cis - 2 - *phenyl* - 4 - t - *butyl* - *cyclohexanone* anti - *phenylhydrazone* (**23**). These products were obtained by reactions of compound **8**, and *cis* - 2 - phenyl - 4 - *t* - butyl - cyclohexanone[2] with $PhNHNH_2$, carried out in anhydrous ether in the presence of

anhydrous Na_2SO_4, at room temperature, with stirring for 2–3 hr. Sodium sulphate was filtered off, and the solvent removed. Physical, analytical, and spectral data are reported in Table 2.

Cycloalkanones (**3, 7, 8, 12, 15a, 15b, 16a, 16b, 19a, 19b, 20a, 20b**). Phenylhydrazones (**2, 6, 11, 14a, 14b, 18a, 18b, 22a**) (0.0025 mol) were dissolved in methanol (50–70 ml) and hydrolysed at pH 7 with sodium periodate as previously described,[2] furnishing ketones (**3, 7, 12, 15a, 15b, 19a, 19b**) respectively. Compounds (**8a, 16a², 16b², 20a, 20b**) were prepared from the corresponding isomers (**7, 15a, 15b, 19a, 19b**) by equilibration in basic medium.[2] All cycloalkanones were obtained in almost quantitative yield. Physical, analytical, and spectral data are reported in Table 3.

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REFERENCES

[1]S. Bozzini, S. Gratton, A. Risaliti, A. Stener, M. Calligaris and G. Nardin, *J. Chem. Soc. Perkin I* 1377 (1977).
[2]S. Bozzini, S. Gratton, G. Pellizer, A. Risaliti and A. Stener, *Ibid.* 869 (1979).
[3]S. Bozzini, B. Cova, S. Gratton, A. Lisini and A. Risaliti, *Ibid.* 240 (1980).
[4]E. J. Corey and D. Enders, *Tetrahedron Letters* 3 (1976).
[5]A. Laaksonen, J. Kowalewski and P. Siegbahn, *Chem. Phys. Lett.* **69**, 109 (1980).
[6]F. Johnson, *Chem. Rev.* **68**, 375 (1968).
[7]F. Johnson and D. T. Dix, *J. Am. Chem. Soc.* **93**, 5931 (1971).
[8]L. Mion, A. Casadevall and E. Casadevall, *Bull. Soc. Chim. Fr.* **7**, 2950 (1968).
[9]F. P. Colonna, E. Valentin, G. Pitacco and A. Risaliti, *Tetrahedron* **29**, 3011 (1973).
[10]M. Yanagita and A. Tahara, *J. Org. Chem.* **18**, 792 (1953).
[11]A. Casadevall, E. Casadevall and M. Lasperas, *Bull. Soc. Chim. Fr.* **11**, 4506 (1968).
[12]R. Belcher, W. Hoyle and T. S. West, *J. Chem. Soc.* 2743 (1958).
[13]S. Brodka and H. Simon, *Chem. Ber.* **102**, 3647 (1969).
[14]E. W. Garbisch, Jr., *J. Org. Chem.* **30**, 2109 (1965).