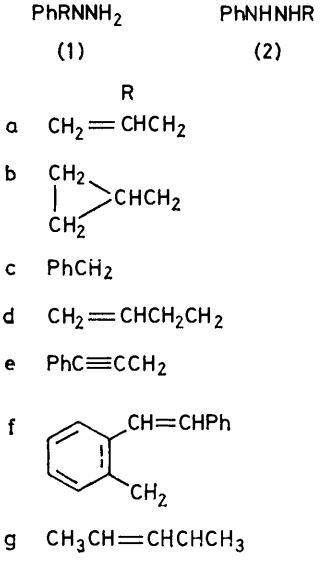
Synthesis and Oxidation of Some 1-Alkenyl-1-phenylhydrazines and their 1,2-Isomers †

By **Anthony J. Bellamy** * and **Lachlan Maclean**, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The synthesis of a series of 1-alkenyl-1-phenylhydrazines by alkylation of the sodium salt of phenylhydrazine is described, this being found to be the most efficient procedure in terms of the utilisation of the alkylating agent. The oxidative rearrangement of 1-allyl-1-phenylhydrazine to 1-phenylazoprop-2-ene is described, together with the results obtained from the oxidation of other related 1-alkenyl-1-phenylhydrazines. 2-Allyl-1-phenylhydrazine has been synthesised in high yield by alkylating the sodium salt of 1,2-diformyl-1-phenylhydrazine, thus giving an easy route to 1-phenylazoprop-2-ene and other phenylazoalkanes which cannot be prepared *via* reduction of the corresponding phenylhydrazones.

THE recent paper by Smith and DeWall [1] in which they describe a detailed study of the site of benzylation of 1-benzyl-1-phenylhydrazine, and of methylation of phenylhydrazine, prompts us to report our own work concerned with the synthesis of a variety of 1-alkenyl-1-phenylhydrazines (1a—g) and their 1,2-analogues (2a, b). The former series of compounds was required for a study of the possible rearrangements [2] which these compounds might exhibit on oxidation to the corresponding diazenes, the results of which are reported at the end of the present paper, while the latter series of compounds was required for the preparation of authentic



samples of the unsaturated phenylazoalkanes which we anticipated might be formed by the oxidative rearrangement of the former series. The general methods which are available for the preparation of these compounds have been adequately reviewed elsewhere.[3,4]

RESULTS AND DISCUSSION

Preparation of 1-*Alkenyl*-1-*phenylhydrazines*.—Our approach focused on the alkylation of phenylhydrazine or a derivative of phenylhydrazine, since this is a direct route (an important factor where the alkylating agent is not readily available) and was applicable to all the compounds we required. Other less direct approaches, *e.g.* direct amination of the appropriate secondary amine, and reduction of the *N*-nitroso-derivative of the secondary amine, were less reliable, and in the latter case gave back considerable quantities of the secondary amine by cleavage of the N–N bond.

As anticipated, the direct alkylation of phenylhydrazine itself using allyl chloride in ether gave a mixture of (1a) and (2a) (4 : 1). Fischer and Knoevenagel [5] originally claimed that this procedure gave (2a), since on oxidation with yellow mercuric oxide the alkylation product gave 1-phenylazoprop-2-ene, but it was subsequently shown by Michaelis and Luxembourg [6] that the alkylation product was largely (1a) and that the 1-phenylazoprop-2-ene arose by an oxidative rearrangement of the corresponding diazene.[2] The direct alkylation of phenylhydrazine with cyclopropylmethyl chloride at 90 °C in the absence of solvent gave 1,2-dialkylation, monoalkylation, and unchanged phenylhydrazine. The monoalkylated component was positively identified as (1b) although (2b) may also be present. Thus direct alkylation of phenylhydrazine suffers from two main limitations, lack of regioselectivity and polyalkylation.

Both these problems can be overcome, however, by using the sodium salt of phenylhydrazine,[7] generated in benzene using sodium hydride. This procedure gave monoalkylation only at N(1), with trace amounts of dialkylation, for compounds (1a—g). Occasionally the product was contaminated with small amounts of unchanged phenylhydrazine. The latter can be detected and quantified in two ways: (*a*) by converting the product to its hydrochloride and examining the latter by i.r. spectroscopy; phenylhydrazine hydrochloride has three diagnostic bands at 887, 857, and 770 cm^{-1} (Nujol); and (*b*) by treating the product with acetone and examining the resulting material (after removing the excess of acetone) by n.m.r. spectroscopy. Typically, two intense singlets were observed at *ca.* δ 2 due to the *cis*- and *trans*-methyl groups of acetone *N*-alkyl-*N*-phenylhydrazone, together with two weak singlets due to the corresponding methyl groups in acetone phenylhydrazone (at δ 1.75 and 2.02 respectively in CCl_4

† No reprints available.

solution).[8] The phenylhydrazine content was estimated from the relative intensities of these two pairs of singlets. (The same technique was also used to differentiate between 1-alkyl-1-phenylhydrazines and 2-alkyl-1-phenylhydrazines in other product mixtures, since the latter do not form condensation products with acetone.) Of the two methods, we feel that the latter technique is probably of greater applicability for indicating the presence of phenylhydrazine.

If residual phenylhydrazine was found to be present, it was readily removed by extracting the crude hydrochloride with boiling benzene, in which the hydrochloride of the 1-alkenyl-1-phenylhydrazine is soluble and phenylhydrazine hydrochloride is not. This procedure worked satisfactorily for compounds (1a—f), but was usually unnecessary. However, when the above extraction procedure was applied to the fairly pure hydrochloride of (1g), the material recovered from the extract was found to be a mixture of the hydrochlorides of (1g) and (2g), with the latter predominating. Furthermore when the residue from the extraction was basified, the amount of phenylhydrazine recovered was significantly higher than the amount anticipated from an analysis of the alkylation product. Thus, the hydrochloride of (1g) is unstable under the extraction conditions, rearranging to the more stable hydrochloride of (2g), probably by a dealkylation–realkylation mechanism (Scheme 1; R = H, R′ = $CH_3CH{=}CHCHCH_3$) as observed by Smith and DeWall [1] for the rearrangement of 1,1-dibenzyl-1-phenylhydrazinium chloride to 1,2-dibenzyl-1-phenylhydrazine hydrochloride (Scheme 1; R = R′ = $PhCH_2$). In the present example a [2,3]-sigmatropic migration is also possible, enabling the hydrochloride of (1g) to be converted directly to the hydrochloride of (2g) (but see later). No analogous instability of the hydrochloride of (1a) was observed.

$$PhRR'\overset{+}{N}H_2\ Cl^- \longrightarrow PhRNNH_2 + R'Cl \longrightarrow PhR\overset{+}{N}NH_2R'\ Cl^-$$

SCHEME 1

When the sodium salt of phenylhydrazine was alkylated with triphenylmethyl chloride the product, not unexpectedly in view of the above rearrangement, was 1-phenyl-2-triphenylmethylhydrazine. This could arise by initial alkylation at N(1), followed by rearrangement *via* either dealkylation–realkylation involving Cl^- or simple [1,2]sigmatropic migration. By comparison, 1-phenyl-1-diphenylmethylhydrazine can be prepared [9] using a similar procedure. Interestingly, an attempt to prepare the hydrochloride of 1-phenyl-2-triphenylmethylhydrazine in ether at 0 °C gave phenylhydrazine hydrochloride and triphenylmethyl chloride. (The hydrochloride of the 1,2-disubstituted hydrazine was obtained by working at a lower temperature.) The hydrochloride of 1-phenyl-1-diphenylmethylhydrazine is also reported to be unstable and undergoes dealkylation.[9]

A further approach to the synthesis of 1-alkyl-1-phenylhydrazines, namely alkylation of t-butyl 2-phenylcarbazate (analogous to the preparation of 1,1-dialkylhydrazines using t-butyl carbazate [10]) was also studied but was unsuccessful when allyl bromide was used as the alkylating agent, the carbazate being recovered unchanged, and gave only limited success when benzyl bromide was used. Because of the low nucleophilicity of the carbazate, high temperature and/or long reaction times were necessary, and under these conditions the t-butyl protecting group was labile. However the product from such a reaction appeared to be largely (1c). This procedure was not investigated further.

Since this work was completed a study of the synthesis of 1-alkyl-1-phenylhydrazines by an improved method for the *N*-alkylation of benzaldehyde phenylhydrazone, followed by hydrolysis of the resulting benzaldehyde *N*-alkylphenylhydrazone, has been reported.[11] This method gave overall yields of 40% for (1a) and 70% for (1c), both being about 20% below the yields obtained in the present work using the more direct alkylation of the sodium salt of phenylhydrazine. A further advantage of our method is that only an equivalent amount of alkylating agent is required; in the *N*-alkylation stage of the above method an excess (1.5—2.0) of the alkylating agent is required.

Preparation of 2-Alkyl-1-phenylhydrazines.—Compound (2b) was prepared by reduction of cyclopropanecarboxaldehyde phenylhydrazone with lithium aluminium hydride, a method which has fairly general applicability.[12] However this method cannot be used when the phenylhydrazone contains other reducible groups, or when the phenylhydrazone cannot be prepared. Such is the case for the preparation of 2-allyl-1-phenylhydrazine; acrylaldehyde phenylhydrazone cannot be isolated, attempted preparations giving 1-phenyl-2-pyrazoline.[5,13] 2-Allyl-1-phenylhydrazine was required for the preparation of an authentic sample of 1-phenylazoprop-2-ene. Examination of the literature revealed only three reports of the preparation of this latter compound, all of which involved the oxidative rearrangement of 1-allyl-1-phenylhydrazine.[2,5,6] Thus no independent, unambiguous preparation of 1-phenylazoprop-2-ene was known.

Since the direct alkylation of phenylhydrazine with allyl bromide had been found to give both the 1,1- and the 1,2-disubstituted hydrazine, the former predominating, we examined the possibility of using either a blocking group to prevent alkylation at N(1), or an activating group to promote alkylation at N(2). Since it had been reported [14] that 2-ethyl-1-phenylhydrazine could be prepared by the alkylation of the sodium salt of 2-formyl-1-phenylhydrazine with ethyl iodide, followed by hydrolysis of the product, we adapted this procedure using allyl bromide instead of ethyl iodide. However the product was a mixture of 1- and 2-allyl-1-phenylhydrazine in approximately equal amounts.

This unexpected result, together with the surprisingly complex ^1H and ^{13}C n.m.r. spectra of the 2-formyl-1-phenylhydrazine, suggested the need for more extensive

characterisation of the latter material. Its formulation as the 1,2-isomer was supported by the observations that it failed to give a hydrazone derivative with acetone (*cf.* 1-acetyl-1-phenylhydrazine), and that acetylation with acetic anhydride followed by selective hydrolysis gave 1-acetyl-1-phenylhydrazine,[15] identified by comparison with an independently prepared sample,[16] and no 2-acetyl-1-phenylhydrazine. The observed simplification of the ^{13}C n.m.r. spectrum of 2-formyl-1-phenylhydrazine at elevated temperatures indicated that the material was a single compound, existing in two preferred conformations in solution. The isolation of both 1,1- and 1,2-disubstituted hydrazines from the alkylation of the sodium salt of 2-formyl-1-phenylhydrazine suggests that proton abstraction by the base takes place at either of the two nitrogen atoms, both positions giving a stabilised anion.

Several attempts were made to separate the two isomeric products, one of which was largely successful. This involved treating the mixture with laevulinic acid, $CH_3COCH_2CH_2CO_2H$. Only the unwanted 1-allyl-1-phenylhydrazine is capable of condensing with the carbonyl group to give a hydrazone, which because of the carboxylic acid group is extractable by base; any phenylhydrazine present would also be removed by this procedure. Although this method served to remove the 1,1-disubstituted hydrazine, the recovered 2-allyl-1-phenylhydrazine was slightly contaminated with unidentified impurities (see Experimental section). Similar results were obtained when the same procedure was used to separate 2-benzyl-1-phenylhydrazine from its 1,1-isomer.

Alkylation of 1-acetyl-1-phenylhydrazine, prepared from the 2-formyl-1-phenylhydrazine above, was also investigated. In this case alkylation with allyl bromide occurred exclusively at N(2), but the product obtained by hydrolysis after reaction for 28 days at 20 °C was a 1 : 1 mixture of 2-allyl-1-phenylhydrazine and phenylhydrazine. This procedure has potential but was not examined further as the desired compound had by this time been prepared by another route (see below).

The alkylation of the sodium salt of 1,2-diformyl-1-phenylhydrazine proved to be the most satisfactory method for preparing 2-allyl-1-phenylhydrazine giving, after hydrolysis, a pure product in 85% yield. Oxidation of the hydrazine with yellow mercuric oxide gave an authentic sample of 1-phenylazoprop-2-ene. 1,2-Diformyl-1-phenylhydrazine also exhibited a temperature-dependent ^{13}C n.m.r. spectrum which was consistent with the adoption of two preferred conformations in solution.

The successful preparation of a 2-alkyl-1-phenylhydrazine by the above method offers an efficient and convenient alternative to the phenylhydrazone reduction method. This procedure was unsuccessful however in the case of (2g) using 2-chloropent-3-ene, but this is believed to be a reflection of the sensitivity of the alkylating agent towards elimination, rather than indicating a significant defect in the general method. The alternative alkylation of 1-acetyl-1-phenylhydrazine may be more successful in such cases.

Oxidation of 1-*Alkenyl*-1-*phenylhydrazines*.—Following from the demonstration that oxidation of 1-allyl-1-phenylhydrazine gave, by [2,3]sigmatropic migration in an intermediate diazene, 1-phenylazopent-2-ene,[2] we wished to investigate the wider applicability of this type of reaction. Consequently we studied the oxidation of compounds (1a—g) and the results of these studies are reported below.

While we were readily able to demonstrate the clean, oxidative rearrangement of (1a) to 1-phenylazoprop-2-ene,[2] the results from compounds (1b) and (1d—f) were disappointing. In none of the cases were the anticipated phenylazo-products formed, and the complex mixtures of products were in most cases consistent with the formation of tetra-substituted tetraz-2-enes and their decomposition products. The diazenes, which were assumed to be generated,[17] appeared to be reluctant to undergo intramolecular rearrangement, and preferred alternative intermolecular processes. The oxidation of (1c) gave 1,4-dibenzyl-1,4-diphenyltetraz-2-ene in high yield, as had previously been reported;[18] the tetrazene underwent some decomposition during purification.

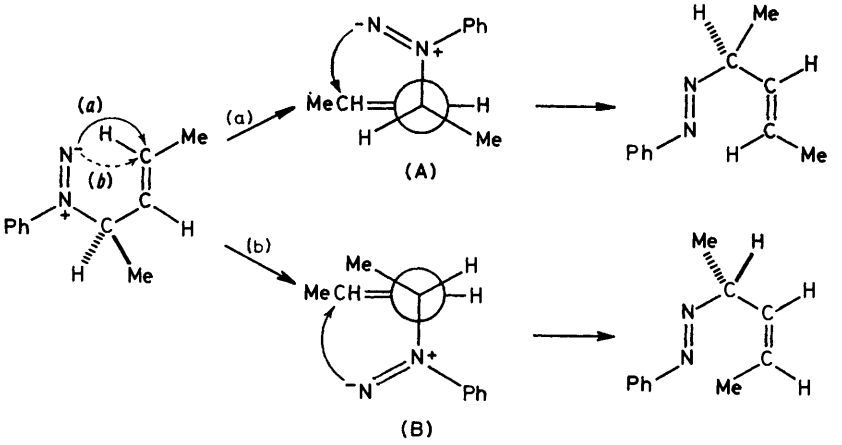
The oxidation of (1g) was more rewarding. The product was a mixture of two components (ratio 1.35 : 1), one of which was identified as *trans*-2-phenylazopent-3-ene by comparison with the oxidation product from 2-(pent-3-en-2-yl)-1-phenylhydrazine, the latter being obtained by rearrangement of the 1,1-disubstituted hydrazine hydrochloride on attempted purification (see earlier). The second, minor component was so similar to the first (*e.g.* n.m.r. spectrum) that the two could not be separated by column chromatography, although they could be resolved by h.p.l.c. After excluding two reasonable possibilities [pent-3-en-2-one phenylhydrazone and *N*-(pent-3-en-2-yl)aniline] for the second component by comparison with the n.m.r. spectra of authentic samples, we propose that the most reasonable structure for this component is *cis*-2-phenylazopent-3-ene. (Geometrical isomerism about the N=N bond is unlikely since the *cis*-isomer would be thermally unstable). Unfortunately catalytic hydrogenation, which should have converted the two components to a common product if this assignment is correct, resulted in considerable over-reduction, although 2-(pent-2-yl)-1-phenylhydrazine and 2-phenylazopentane (resulting from air oxidation of the former) were both identified in the product mixture.

A [2,3]sigmatropic migration in the diazene generated from (1g) should in fact produce two products, isomeric about the C=C bond, from the two alternative suprafacial–suprafacial modes of migration (Scheme 2), the relative amounts of the two products reflecting that of the conformers (A) and (B). Conformer (A) (most stable) on rearrangement would give *trans*-2-phenylazopent-3-ene (major product) while conformer (B) would give *cis*-2-phenylazopent-3-ene. This situation was not identifiable in any of the previously studied diazenes,[2]

but has obvious close analogy with the [2,3]sigmatropic migration (Wittig rearrangement) of the anion derived from the benzyl ether of (S)-(+)-*trans*-pent-3-en-2-ol, which gave *trans*- and *cis*-2-methyl-1-phenylpent-3-en-1-ol (83 : 17), both of which were chiral and had opposite configurations at C(2).[19]

It was anticipated at the outset that if (1g) gave 2-phenylazopent-3-ene, then using chiral (1g) it might be possible to produce chiral 2-phenylazopent-3-ene by asymmetric induction, and hence chiral 2-phenylazopentane, the latter being required for studies on the chemistry of phenylazoalkanes.[20] Asymmetric induction in some [2,3]sigmatropic migrations is known to be highly efficient.[19,21] Since the two geometrical isomers produced by rearrangement of the diazene from (1g) are present in roughly equal amounts and are not readily separable, hydrogenation of the C=C bond in the mixture of products derived from chiral (1g) would give material which was almost racemic. This follows from a consideration of Scheme 2; with complete asymmetric induction during the rearrangement, *trans*-2-phenylazopent-3-ene would possess the opposite configuration at C(2) to *cis*-2-phenylazopent-3-ene, and this would produce enantiomeric molecules in roughly equal amounts once the geometrical difference at the C=C bond has been removed. Thus the planned route to a chiral, secondary phenylazoalkane would only succeed if the geometric isomers could be separated.

The formation of two, geometrically isomeric products would also be expected in the rearrangement of the hydrochloride of (1g) to the hydrochloride of (2g), if the rearrangement occurred by a [2,3]sigmatropic migration. Since only one isomer was observed, the rearrangement most probably occurs *via* a dealkylation–realkylation mechanism (Scheme 1; R = H, R′ = CH_3CH=CH-$CHCH_3$).[1]



SCHEME 2

EXPERIMENTAL

N.m.r. spectra were measured at 100 MHz on $CDCl_3$ or CCl_4 solutions unless otherwise stated.

Preparation of 1-Alkylphenylhydrazines by Alkylation of the Sodium Salt of Phenylhydrazine.—(*i*) *Preparation and alkylation of the sodium salt of phenylhydrazine.* A mixture of equimolar amounts (0.1 mol) of sodium hydride and phenylhydrazine in dry benzene (150 ml) was stirred under nitrogen at 70 °C for 2—7 h, to give the sodium salt as a yellow-brown precipitate. The reaction was cooled to 20 °C, an equimolar amount of the alkyl halide was added, and the mixture was stirred for 12 h at 20 °C, and then refluxed for 3—4 h. The precipitated sodium halide was removed either by filtration through Celite or by washing with water, and the organic layer was concentrated.

(*ii*) *Removal of phenylhydrazine.* When phenylhydrazine was found to be present (see Discussion section) it was removed as follows. Dry, gaseous hydrogen chloride was passed into a solution of the alkylation product in dry ether (0.1 mol in 200 ml) at 0 °C for 7—10 min. The precipitated hydrochloride was filtered off, washed with ether, and sucked dry. The filtrate was evaporated to give a further quantity of hydrochloride in the form of a dirty white solid or a green-brown gum which solidified in some cases. The total yield of hydrochloride was 80—85%; only about half was recovered in the initial precipitate. The combined hydrochloride was exhaustively extracted with boiling benzene, and the combined extracts were concentrated and basified with 20% aqueous sodium carbonate solution to give the pure 1-alkyl-1-phenylhydrazine. The residue of the benzene extraction, when similarly basified gave mainly phenylhydrazine with a small amount of the 1-alkyl-1-phenylhydrazine. The following 1-alkyl-1-phenylhydrazines were prepared by this procedure.

1-*Allyl*-1-*phenylhydrazine* (1a). From allyl bromide (57%), uncontaminated by phenylhydrazine; δ 3.45 (s, NH_2), 3.9—4.0 (m, CH_2CH=CH_2), 5.05—5.3 (m, CH_2CH=CH_2), 5.6—6.0 (m, CH_2CH=CH_2), and 6.6—7.3 (m, 5 H, aromatic); the hydrochloride (from benzene) had m.p. (sealed tube) 148—151 °C (lit.,[22] m.p. 149—150 °C). After several weeks the hydrochloride had developed a purple colour where it had been exposed to sunlight.

1-*Cyclopropylmethyl*-1-*phenylhydrazine* (1b). From cyclopropylmethyl chloride[23] (prepared *via* cyclopropylmethanol[24]) (57%); δ 0.1—1.3 (m, 5 H, cyclopropyl), 3.1—3.16 (d, *J* 6 Hz, $C_3H_5CH_2$), 3.4 (s, NH_2), and 6.5—7.22 (m, 5 H, aromatic); the hydrochloride (from benzene) had

m.p. (sealed tube) 135—138 °C. The hydrochloride developed a pale brown colour after several weeks.

1-*Benzyl*-1-*phenylhydrazine* (1c). From benzyl bromide (87%), uncontaminated by phenylhydrazine; δ 3.28 (s, NH_2), 4.46 (s, PhCH_2), and 6.5—7.3 (m, 10 H, aromatic); the hydrochloride (from benzene) had m.p. (sealed tube) 170—172 °C (lit.,[25] m.p. 176—177 °C). After several weeks the hydrochloride had developed a purple colour where it had been exposed to sunlight.

1-(*But*-3-*enyl*)-1-*phenylhydrazine* (1d). From 1-bromobut-3-ene (80%), uncontaminated by phenylhydrazine; δ 2.2—2.45 (m, $CH_2CH_2CH{=}CH_2$), 3.3—3.46 (m, $CH_2CH_2CH{=}CH_2$), 3.47 (s, NH_2), 4.92—5.2 (m, $CH_2CH_2CH{=}CH_2$), 5.58—6.04 (m, $CH_2CH_2CH{=}CH_2$), and 6.58—7.35 (m, 5 H, aromatic); the hydrochloride (from benzene) had m.p. (sealed tube) 102—105 °C.

1-(3-*Phenylprop*-2-*ynyl*)-1-*phenylhydrazine* (1e). From 1-bromo-3-phenylprop-2-yne [26,27] (prepared *via* 3-phenylprop-2-yn-1-ol [28]) (89%), uncontaminated by phenylhydrazine; δ 3.76 (s, NH_2), 4.35 (s, CH_2), and 6.7—7.6 (m, 10 H, aromatic); the hydrochloride (from benzene) had m.p. (sealed tube) 161—164 °C.

1-(2-*Styrylphenylmethyl*)-1-*phenylhydrazine* (1f). From 2-styrylphenylmethyl chloride [29] (86%), m.p. 93—95 °C (unrecrystallised), uncontaminated by phenylhydrazine; δ 3.45 (s, NH_2), 4.6 (s, CH_2), and 6.7—7.7 (m, 16 H, aromatic and olefinic); the hydrochloride (from benzene) had m.p. (sealed tube) 177—179 °C; *m/e* 300 $[P - HCl]^+$, and 193. The 2-styrylphenylmethyl chloride was prepared starting from phthalic anhydride *via* benzalphthalide,[30] benzylphthalide,[31] stilbene-2-carboxylic acid,[31] and 2-styrylphenylmethanol.[29]

1-(*Pent*-3-*en*-2-*yl*)-1-*phenylhydrazine* (1g). From 2-chloropent-3-ene [32] (prepared from *trans*-pent-3-en-2-ol [33]) (83%); δ 1.18—1.35 (d, *J* 6 Hz, $CH_3CHCH{=}CHCH_3$), 1.55—1.85 (m, $CH{=}CHCH_3$), 3.15—3.60 (br s, NH_2), 4.2—4.5 (m, $CH_3CHCH{=}CHCH_3$), 5.2—5.8 (m, $CH{=}CH$), and 6.55—7.45 (m, 5 H, aromatic); the hydrochloride (crude) had m.p. (sealed tube) 207—209 °C. The diagnostic i.r. bands for phenylhydrazine hydrochloride, if present, were obscured by other absorptions. When the hydrochloride was subjected to the benzene extraction procedure, the recovered free hydrazine was found (n.m.r.) to be a mixture of the original hydrazine and the isomeric 2-alkyl-1-phenylhydrazine; the isomerisation was complete after refluxing the extract for 3 days. The latter assignment was made on the basis of its n.m.r. spectrum, which was very similar to that of the 1-alkyl-1-phenylhydrazine except for the $CH_3CHCH{=}CHCH_3$ absorptions, and its ready oxidation to the corresponding azo-compound either with air or mercuric oxide. The azo-compound obtained in this case was a single isomer (*cf.* the azo-products formed by oxidation of the 1-alkyl-1-phenylhydrazine, see below). The 2-(pent-3-en-2-yl)-1-phenylhydrazine (2g) had δ 1.05—1.2 (d, *J* 6 Hz, $CH_3CHCH{=}CHCH_3$), 1.6—1.8 (doublet with fine splitting, *J ca.* 6 Hz, $CH{=}CH{\cdot}CH_3$), 3.15—3.5 (m, $CH_3CHCH{=}CHCH_3$), 3.7—4.6 (br s, NH_2), 5.02—5.8 (m, $CH{=}CH$), and 6.52—7.36 (m, 5 H, aromatic). The 2-phenylazopent-3-ene, obtained by oxidation of the 2-alkyl-1-phenylhydrazine, was purified by dry column chromatography to give a mobile, orange-yellow liquid; δ 1.34—1.52 (d, *J* 6 Hz, $CH_3CHCH{=}CHCH_3$), 1.68—1.8 (d, *J* 6 Hz, $CH{=}CHCH_3$), 4.1—4.5 (m, $CH_3CHCH{=}CHCH_3$), 5.6—5.82 (m, $CH{=}CH$), and 7.22—7.75 (m, 5 H, aromatic). The quantity of phenylhydrazine recovered from the extraction procedure (17%) was significantly higher than the amount anticipated from the analysis of the alkylation product.

1-*Phenyl*-2-*triphenylmethylhydrazine*.— Triphenylmethyl chloride (0.03 mol) and phenylhydrazine (0.06 mol) in ether (170 ml) were refluxed under nitrogen for 1.5 h. The white precipitate was filtered off and the filtrate was concentrated to give the crude product (100%), m.p. 136—137 °C (from benzene) (lit.,[34] m.p. 136—137 °C); δ 4.1 (br s, NH), 4.5 (br s, NH), and 6.7—7.6 (br m, 20 H, aromatic); *m/e* 350 (P^+). An attempted preparation of the hydrochloride derivative at 0 °C in ether gave phenylhydrazine hydrochloride and triphenylmethyl chloride, but at −10 °C the derivative was obtained satisfactorily.

The attempted preparation of 1-phenyl-1-triphenylmethylhydrazine by alkylation of the sodium salt of phenylhydrazine using triphenylmethyl chloride also gave crude 2-alkyl-1-phenylhydrazine.

1-*Cyclopropyl*(*phenylazo*)*methane*.—This was prepared by reduction of cyclopropanecarbaldehyde phenylhydrazone with lithium aluminium hydride in tetrahydrofuran, followed by oxidation of the resulting 2-alkyl-1-phenylhydrazine with yellow mercuric oxide.[12] It was a bright yellow liquid (80%); δ 0.2—1.7 (m, C_3H_5), 3.75—3.9 (d, *J* 7 Hz, $C_3H_5CH_2$), and 7.1—7.8 (m, 5 H, aromatic).

2-*Formyl*-1-*phenylhydrazine*.—The method of de Vries,[35] which involved treating phenylhydrazine with formic acid, was used. The product (70%) had m.p. 143—144 °C (from ethanol–ether) (lit.,[35] m.p. 144—145 °C). Both the ^1H and ^{13}C n.m.r. spectra in $(CD_3)_2SO$ at 25 °C were more complex than anticipated: δ_H 6.35—7.50 (m), 7.6—8.4 (m), 9.32 (s), 9.54 (s), and 9.68 (br s), ratio 94 : 35 : 3 : 2 : 9; δ_C 112.370, 112.515, 118.829, 119.624, 128.865, 129.109, 148.846, 149.571, 160.708, and 167.817. At 181 °C, the ^{13}C spectrum was simplified from ten to five lines, δ_C 113.421, 119.917, 128.814, 148.931, and 163.160, as expected for 2-formyl-1-phenylhydrazine. The ten-line spectrum reappeared on cooling to 25 °C.

Further characterisation of 2-formyl-1-phenylhydrazine was achieved by (*i*) treatment with acetone, when the material was recovered unchanged (*cf.* 1-acetyl-1-phenylhydrazine which forms a hydrazone with acetone); (*ii*) treatment with acetic anhydride (1 equiv.) at 100 °C for 1 h; [15] after controlled hydrolysis with concentrated hydrochloric acid (7 h at 25 °C) 1-acetyl-1-phenylhydrazine, m.p. 124—125 °C (from ethanol–ether) (lit.,[15] m.p. 124 °C), was obtained which was identical to an authentic sample prepared by amination of acetanilide.[16]

Alkylation of the Sodium Salt of 2-*Formyl*-1-*phenylhydrazine with Allyl Bromide*.—A solution of 2-formyl-1-phenylhydrazine (0.06 mol) in hot 1,2-dimethoxyethane (100 ml) was added in one portion to a stirred suspension of sodium hydride (0.06 mol) in 1,2-dimethoxyethane (20 ml). After stirring for 3.5 h under nitrogen, a clear, bright orange solution had formed and allyl bromide (0.06 mol) was added in one portion. The mixture was stirred for 26 h; the white precipitate which formed was filtered off, and the filtrate was concentrated. The alkylation product (10.65 g) was stirred with concentrated hydrochloric acid (40 ml) for 20 h, water was added to dissolve the hydrochloride which had separated, and the solution was extracted with ether to remove any unhydrolysed material. The aqueous solution was basified with 20% aqueous sodium carbonate solution and extracted with chloroform. The product was isolated as a clear liquid (8.12 g); the n.m.r. spectrum indicated that it was a mixture of 1-allyl- and

2-allyl-1-phenylhydrazine in approximately equal amounts. The presence of the 1,1-isomer was confirmed by treating a sample of the product with acetone.

Alkylation of the sodium salt of 2-formyl-1-phenylhydrazine with benzyl bromide also gave both the 1,1- and the 1,2-derivatives (3 : 2).

The mixture of 1-allyl- and 2-allyl-1-phenylhydrazine (0.02 mol) and laevulinic acid (0.02 mol) in ethanol (20 ml) was refluxed for 20 h. The solvent was evaporated off and the residue was treated with a saturated aqueous solution of potassium carbonate (50 ml), followed by extraction with ether. Concentration of the organic layer, and distillation at 70—72 °C/0.05 mmHg, gave a mobile, yellow-brown liquid (0.5 g) which was largely 2-allyl-1-phenylhydrazine. Apart from signals due to the 1,2-disubstituted hydrazine, the n.m.r. spectrum also exhibited resonances at δ 1.04—2.76 which integrated to 0.6 protons (relative to the hydrazine). Furthermore the i.r. spectrum exhibited unexpected peaks at $\nu_{max.}$ 1 765 and 1 720 cm^{-1}.

When this procedure was applied to the separation of 1-benzyl- and 2-benzyl-1-phenylhydrazine similar results were obtained.

Alkylation of 1-*Acetyl*-1-*phenylhydrazine with Allyl Bromide*.—A solution of 1-acetyl-1-phenylhydrazine (0.05 mol) and allyl bromide (0.002 5 mol) in chloroform (6 ml, B.D.H. AnalaR) was stirred at 20 °C under nitrogen for 28 days. The white precipitate was filtered off and the filtrate was concentrated. The residue (0.59 g) was hydrolysed by heating under reflux with 3M hydrochloric acid (30 ml) for 3 h. Isolation of the product gave a mixture (0.23 g) of 2-allyl-1-phenylhydrazine and phenylhydrazine in approximately equal amounts.

1,2-*Diformyl*-1-*phenylhydrazine*.—The method of Freund and Horst [36] was used. The product (90%) had m.p. 125—126 °C (from benzene) (lit.,[36] m.p. 126 °C). Both the ^1H and ^{13}C n.m.r. spectra in $(CD_3)_2SO$ at 25 °C were more complex than anticipated: δ_H 7.05—7.6 (m), 8.34 (s), 8.42 (s), and 8.84 (s), ratio 60 : 8 : 3 : 5; δ_C 119.723, 120.121, 121.073, 121.420 (w), 126.025, 126.381, 128.444 (w), 128.960, 129.553, 139.452, 140.590, 159.611, 160.013, 161.491, 161.706 (w), 163.850, and 167.282. At 155 °C the ^{13}C spectrum was simplified from 17 to 6 lines; δ_C 121.255, 126.148, 129.109, 140.702, 161.259, and 161.450 as expected for 1,2-diformyl-1-phenylhydrazine. The 17-line spectrum reappeared on cooling to 25 °C.

Alkylation of the Sodium Salt of 1,2-*Diformyl*-1-*phenylhydrazine with Allyl Bromide*.—A solution of 1,2-diformyl-1-phenylhydrazine (0.02 mol) in hot 1,2-dimethoxyethane (50 ml) was added to a stirred suspension of sodium hydride in 1,2-dimethoxyethane (20 ml), and the mixture was refluxed under nitrogen for 7 h. After cooling, allyl bromide (0.02 mol) was added and the mixture was refluxed with stirring for a further 6 h. The alkylation product was isolated and hydrolysed by stirring with concentrated hydrochloric acid (40 ml) for 18 h. After washing with ether, the aqueous solution was basified with 20% aqueous sodium carbonate solution and extracted with ether. Concentration of the extract gave 2-allyl-1-phenylhydrazine (85%), b.p. 85—86 °C at 0.05 mmHg (lit.,[5] b.p. 172 °C at 60 mmHg); δ 3.22—3.45 (m, $CH_2CH{=}CH_2$), 4.0—4.5 (br s, NHNH), 5.02—5.35 (m, $CH_2CH{=}CH_2$), 5.56—6.04 (m, $CH_2CH{=}CH_2$), and 6.65—7.32 (m, 5 H, aromatic); *m/e* 148 (P^+), 107 (B), and 77.

Oxidation of 2-allyl-1-phenylhydrazine with yellow mercuric oxide in chloroform gave 1-phenylazoprop-2-ene which was identical to the oxidation product from 1-allyl-1-phenylhydrazine (i.r. and n.m.r. spectra).

Oxidation of 1-*Alkyl*-1-*phenylhydrazines*.—(a) *With yellow mercuric oxide*. A 3 : 1 molar ratio of yellow mercuric oxide to hydrazine was used and the concentration of hydrazine was 0.15—6.5 mmol ml^{-1}. The hydrazine was added in one portion to a suspension of the oxidising agent in either ether, chloroform, or methylene chloride. The mercuric oxide soon developed a green colour, but the mixture was stirred under nitrogen in the dark for not less than 18 h. The mixture was filtered through Celite and the product was isolated by evaporation of the solvent.

(b) *With lead tetra-acetate*. Lead tetra-acetate was supplied as a paste with glacial acetic acid. The acetic acid was removed by suction filtration under dry nitrogen on a sintered glass funnel, the solid was washed with dry ether, and the dry oxidising agent was rapidly weighed and used immediately. A solution of the hydrazine (3 mmol) in purified [37] methylene chloride (30 ml) was added during 15 min to a stirred solution of lead tetra-acetate (3.5 mmol) in methylene chloride (30 ml). The mixture was stirred under nitrogen in the dark for a further 25 min before it was filtered through Celite. The filtrate was washed with aqueous sodium hydrogencarbonate solution and then concentrated.

1-*Allyl*-1-*phenylhydrazine*. This gave 1-phenylazoprop-2-ene using mercuric oxide and lead tetra-acetate (100 and 71% respectively). The product was identified by comparison (i.r. and n.m.r. spectra, t.l.c.) with the sample obtained by oxidation of 2-allyl-1-phenylhydrazine; δ 4.55—4.8 (m, $CH_2CH{=}CH_2$), 5.1—5.5 (m, $CH_2CH{=}CH_2$), 5.8—6.6 (m, $CH_2CH{=}CH_2$), and 7.1—7.8 (m, 5 H, aromatic).

1-*Benzyl*-1-*phenylhydrazine*. This gave 1,4-dibenzyl-1,4-diphenyltetraz-2-ene (80%), m.p. 145 °C (from ethanol) (lit.,[38] m.p. 145 °C), which was identical to an authentic sample,[38] using mercuric oxide. No 2-phenylazotoluene or benzaldehyde phenylhydrazone was detected in the crude product using i.r. and n.m.r. spectroscopic analysis. Considerable decomposition of the tetrazene occurred during the reaction and/or work-up and recrystallisation, and when a solution of the tetrazene in xylene was refluxed for 1 h the product was *N*-benzylaniline, *cf.* the oxidation of 1,1-dibenzylhydrazine [39,40] and the decomposition of tetrabenzyltetraz-2-ene.[39,41]

1-*Cyclopropylmethyl*-1-*phenylhydrazine*. This gave 1,4-*biscyclopropylmethyl*-1,4-*diphenyltetraz*-2-*ene* (70%), m.p. 95.5—96.5 °C (from ethanol) using mercuric oxide, and the tetrazene plus its decomposition products using lead tetra-acetate. The tetrazene had δ 0.0—1.5 (m, C_3H_5), 3.98—4.05 (d, *J* 6 Hz, $C_3H_5CH_2$), and 6.2—7.4 (m, 10 H, aromatic); *m/e* 320 (P^+ and B), 292 ($[P - N_2]^+$), and 237 ($[P - C_4H_7]^+$); accurate mass of parent ion 320.200 153 ($C_{20}H_{24}N_4$ requires 320.200 087). No signals attributable to the but-3-enyl group were observed in the n.m.r. spectrum of the crude product.

1-(*But*-3-*enyl*)-1-*phenylhydrazine*. This on oxidation with mercuric oxide gave a crude product which was most probably the corresponding tetrazene (*m/e* 320) and its decomposition products. No cyclopropyl(phenylazo)-methane was present. Both 1-(3-phenylprop-2-ynyl)-1-phenylhydrazine and 1-(2-styrylphenylmethyl)-1-phenylhydrazine gave complex product mixtures on oxidation with mercuric oxide; the anticipated phenylazo-products were not detected.

1-(*Pent*-3-*en*-2-*yl*)-1-*phenylhydrazine*. This on oxidation

with mercuric oxide in chloroform, lead tetra-acetate in methylene chloride, or *p*-benzoquinone in ethanol, gave an orange-yellow, mobile liquid (>90%), which was a mixture of two components [1.35 : 1, h.p.l.c. on silica (7 μm), eluant hexane]. The mixture could not be separated by t.l.c. or wet column chromatography. The n.m.r spectrum of the mixture exhibited both phenyl and pent-3-en-2-yl absorptions (5 H : 9 H); the pent-3-en-2-yl absorptions were analysable in terms of two pent-3-en-2-yl groups with very similar spectra, the most marked differences being the $CH_3CHCH{=}CHCH_3$ absorptions. One set of pent-3-en-2-yl absorptions (major isomer) were identical to those for the 2-phenylazopent-3-ene obtained on oxidation of 2-(pent-3-en-2-yl)-1-phenylhydrazine (formed by rearrangement of the hydrochloride of the 1,1-isomer; see above). We therefore assign this set of absorptions to *trans*-2-phenylazopent-3-ene, and the second set to *cis*-2-phenylazopent-3-ene: *trans*-isomer, δ 1.3—1.45 (d, *J* 6 Hz, $CH_3CHCH{=}CHCH_3$), 1.5—1.75 (m, $CH_3CHCH{=}CHCH_3$), 4.1—4.45 (m, $CH_3CHCH{=}CHCH_3$), 5.4—5.95 (m, CH=CH), and 7.05—7.7 (m, 5 H, aromatic); *cis*-isomer, 1.3—1.45 (d, *J* 6 Hz, $CH_3CHCH{=}CHCH_3$ (0.015 p.p.m. upfield from the corresponding absorption in the *trans*-isomer), 1.5—1.75 (m, $CH_3CHCH{=}CHCH_3$), 4.5—4.85 (m, $CH_3CHCH{=}CHCH_3$), 5.4—5.95 (m, CH=CH), and 7.05—7.7 (m, 5 H, aromatic); *m/e* 174 (P^+), 159, 105 (B), and 77; $\nu_{max.}$ (film) 965 (*trans*-CH=CH) and 730 cm^{-1} (*cis*-CH=CH). Two other reasonable possibilities for the minor component, pent-3-en-2-one phenylhydrazone and *N*-(pent-3-en-2-yl)aniline, the latter being a likely decomposition product of the corresponding tetrazene (*cf.* the tetrazene from 1c), were excluded by the preparation of authentic samples of these compounds.

Hydrogenation of the above product mixture over 10% Pd–C in ethanol at atmospheric pressure was stopped after the uptake of 2 mol equivalents of hydrogen; a hydrogenation which was allowed to continue absorbed over twice this amount. The i.r. spectrum of the product showed that both the absorptions attributed to CH=CH above had disappeared, and an NH absorption had appeared (3 290 cm^{-1}). The n.m.r. spectrum suggested that at least three components were present, two of which were identified as 2-(pent-2-yl)-1-phenylhydrazine and 2-phenylazopentane, the latter being presumably formed by air oxidation of the former; no *trans*-2-phenylazopent-3-ene remained, but it was not possible to decide whether the *cis*-isomer had been removed since the position of its most diagnostic signal (CH_3CH) was now obscured by a broad singlet (δ 4.6—5.1). Other less diagnostic absorptions of the pent-3-en-2-yl group were still present and comparison of these with those of 2-(pent-3-en-2-yl)-1-phenylhydrazine supported the possibility that the third component was this hydrazine.

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