501. *Studies on the Possible Interconversion of Phenylhydrazones and Phenylazoalkanes. Part I* *

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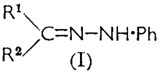
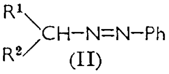
The reported tautomerism between phenylhydrazones and phenylazoalkanes in non-polar solvents has been re-investigated. We have found no evidence for this tautomerism and attribute the observations of other workers to the autoxidation of phenylhydrazones.

The problem concerning the tautomerism between phenylhydrazones and phenylazoalkanes,[1] and the question as to which of the two forms is the more stable if an equilibrium does exist between the two, have remained unsettled for many years.[2] In 1906, Baly and Tuck [3] reported that phenylhydrazones (I) in solution, on irradiation with ultraviolet light, are transformed into the corresponding phenylazoalkanes (II), the latter being the more stable of the two isomeric groups. Since then there has been a controversy as to whether the conclusions of Baly and Tuck were correct,[2] other workers [4] claiming that the phenylhydrazone form was the more stable and that tautomerism into the phenylazoalkane did not occur. Recently, O'Connor [1] attempted to clarify the situation by studying the problem with the aid of several physical techniques. From his results he concluded that in neutral solution phenylhydrazones rapidly tautomerise to phenylazoalkanes.



(I)



(II)

In the course of an investigation into the chemistry of phenylazoalkanes, we had cause to repeat much of O'Connor's work and our results disagree with those reported by him. Our inability to isolate any phenylazoalkanes from solutions of the phenylhydrazones of simple aldehydes and ketones in hexane or carbon tetrachloride has prompted us to publish our experimental results in more detail than would otherwise be necessary.

Since phenylazoalkanes (II) exhibit light absorption in the visible as well as in the ultraviolet region of the spectrum, their formation by the tautomerism of phenylhydrazones in solution should be accompanied by change of the solution from colourless to bright yellow. O'Connor [1] used this fact in an attempt to follow the rearrangement spectroscopically. The rearrangement of cyclohexanone phenylhydrazone (I; $R^1R^2 = -[CH_2]_5-$) to phenylazocyclohexane (II; $R^1R^2 = -[CH_2]_5-$) in hexane (6×10^{-3}M) was reported [1] to have been followed in this manner, the reaction going to completion in 7 minutes. The product was isolated and identified as phenylazocyclohexane. The same rearrangement in carbon tetrachloride was much slower and, in general, aldehyde phenylhydrazones were reported to rearrange much more slowly than ketone phenylhydrazones.

We found that solutions of cyclohexanone phenylhydrazone and acetone phenylhydrazone remain colourless when stored under nitrogen. Indeed, the phenylhydrazones were recovered unchanged after these solutions had been left for 3 months. The possibility that the formation of phenylazoalkanes might be dependent upon the presence of some impurity, for example, water or phenylhydrazine, was eliminated when the experiments were performed in the presence of small amounts of these impurities. Again the solutions remained colourless when stored under nitrogen.

However, when no attempt was made to exclude oxygen from the system, the solutions of phenylhydrazones in hexane or carbon tetrachloride became yellow in a few minutes.

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* Part of this work has been reported in a preliminary Communication, *Chem. and Ind.*, 1964, 1575.

[1] R. O'Connor, *J. Org. Chem.*, 1961, **26**, 4375.

[2] See ref. 1 for a detailed description of the development of this controversy.

[3] E. C. C. Baly and W. B. Tuck, *J.*, 1906, **90**, 982.

[4] P. Ramart-Lucas, J. Hoch, and M. Martynoff, *Bull. Soc. chim. France*, 1937, **4**, 481.

The yellow solutions had spectra which were similar to those of phenylazoalkanes and the strength of the absorption in the visible region was found to be dependent upon the amount of oxygen allowed into the system. Quantitative experiments showed that one mole of oxygen was being absorbed per mole of phenylhydrazone (Table 1). For example, acetone phenylhydrazone absorbed 1·00 mole of oxygen during 3 minutes. Cyclohexanone phenylhydrazone was the most reactive phenylhydrazone studied, the reaction being complete in 2 minutes. In this case, a more accurate value of the uptake was obtained using air instead of pure oxygen. Aldehyde phenylhydrazones reacted at a slower rate than did the ketone phenylhydrazones, as shown in Table 1.

TABLE 1

Quantitative oxygenation of phenylhydrazones

Compound	Solvent	Total uptake of oxygen (moles)	Time of complete reaction (min.)
Acetone phenylhydrazone	Hexane	1·00	3
	$CHCl_3$	0·96	10
Cyclohexanone phenylhydrazone	Hexane	0·95	2
	Hexane	1·01 [a]	3
	Hexane	0·96 [b]	10
	CCl_4	0·96	10
	$CHCl_3$	0·99	4
	MeOH	0·96	100
	MeOH	0·97 [c]	20
n-Butyraldehyde phenylhydrazone	Hexane	0·98	4
	$CHCl_3$	0·60	4
α-Acetaldehyde phenylhydrazone	Hexane	0·96	10
	$CHCl_3$	0·44	12
β-Acetaldehyde phenylhydrazone	Hexane	0·98	9
Butan-2-one *p*-nitrophenylhydrazone	$CHCl_3$	0·61	70

[a] Air used instead of pure oxygen. [b] Reaction performed in the dark. [c] Benzoyl peroxide (1 mg.) used as catalyst.

In carbon tetrachloride, the rate of oxygenation of cyclohexanone phenylhydrazone was slower than in hexane, and in methanol the rate was extremely slow, although one mole of oxygen was still absorbed. Even when benzoyl peroxide was used as a catalyst, the rate of oxygenation of cyclohexanone phenylhydrazone in methanol was still below the value for hexane and carbon tetrachloride. When cyclohexanone phenylhydrazone in hexane was oxygenated in the dark, the reaction was slower than the reaction under normal conditions, but one mole of oxygen was still absorbed showing photo-initiation to be relatively unimportant.

In chloroform, both acetone phenylhydrazone and cyclohexanone phenylhydrazone absorbed one mole of oxygen, although at slightly slower rate than in hexane. The aldehyde phenylhydrazones, however, all absorbed considerably less than one mole of oxygen with the production of red solutions instead of the usual yellow solutions. This result is still being investigated. Butanone *p*-nitrophenylhydrazone in chloroform absorbed a significant amount of oxygen, although rather slowly. In contrast, O'Connor and Rosenbrook [5] reported this compound to be stable to tautomeric change.

The possibility that the phenylhydrazones were rearranging to phenylazoalkanes and that the latter were reacting with oxygen was eliminated when phenylazocyclohexane was recovered quantitatively after treatment of a solution in hexane with oxygen.

Results on the autoxidation of phenylhydrazones, similar to those described above, have been reported previously. Baly and Tuck [3] had explained the yellow coloration in solutions of phenylhydrazones, on irradiation with ultraviolet light, on the basis of tautomerism to the phenylazoalkane isomers. In 1913, Stobbe and Nowak [6] claimed that the basis of Baly and Tuck's explanation was wrong and discovered that a neutral solution of

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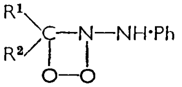
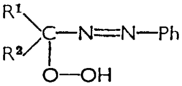
[5] R. O'Connor and W. Rosenbrook, *J. Org. Chem.*, 1961, **26**, 5208.

[6] H. Stobbe and R. Nowak, *Ber.*, 1913, **46**, 2887.

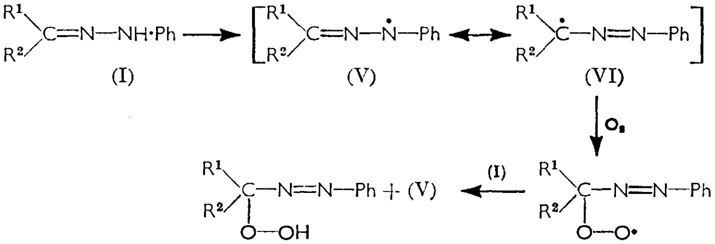
acetaldehyde phenylhydrazone remained colourless if stored under carbon dioxide. If air was not excluded from the system, the solution became yellow and the spectrum of the solution was similar to that reported by Baly and Tuck,[3] and also similar to that of phenylazoethane (II; $R^1 = Me$, $R^2 = H$). However, no phenylazoethane was isolated on evaporation and Stobbe and Nowak concluded that the colour change was due to an oxidation process.

In 1914, Busch and Dietz [7] described the isolation of crystalline products formed during the treatment of benzene solutions of benzaldehyde arylhydrazones with oxygen. However, the structure (III) they proposed for these peroxidic products did not account for their yellow colour.


(III)


(IV)

These products were later re-investigated by Pausacker [8] and by Criegee and Lohous.[9] These workers independently proposed the structure (IV), possessing hydroperoxide and phenylazo-groups, for the autoxidation products of both aliphatic and aromatic phenylhydrazones, the revised structure accounting for the yellow colour. They also suggested a radical mechanism for the autoxidation process, the original source of the radicals being uncertain:



Consistent with this mechanism is the fact that 1-methyl-1-phenylhydrazones do not react with oxygen.

Our own results substantiate structure (IV) for the autoxidation products. 1-Hydroperoxy-1-phenylazocyclohexane (IV; $R^1R^2 = -[CH_2]_5-$), an unstable, yellow, viscous liquid, which was obtained on evaporation of a solution of cyclohexanone phenylhydrazone in hexane after treatment with oxygen, had infrared bands at $\nu_{max.}$ (film) 3400s (broad), 875m, 855m, and 830m cm.$^{-1}$. Similarly, 2-hydroperoxy-2-phenylazopropane (IV; $R^1 = R^2 = Me$), also an unstable, yellow, viscous liquid obtained from acetone phenylhydrazone in hexane, had $\nu_{max.}$ (film) 3400s (broad), 875m, and 850m cm.$^{-1}$. These bands are thought to be characteristic of the hydroperoxide group, which is reported [10] to have strong characteristic absorption at 3550 (broad, O–H stretching) and around 830 cm.$^{-1}$ (O–OH stretching); t-butyl hydroperoxide has $\nu_{max.}$ (film) 3520s (broad), 889m, and 846s cm.$^{-1}$).

The ultraviolet spectra of the 1-hydroperoxy-1-phenylazoalkanes (IV) (Table 2) were typical of simple phenylazoalkanes. The compounds for these measurements were prepared in hexane solution from the corresponding phenylhydrazones, and were not isolated. The spectra of simple phenylazoalkanes (II) (Table 3) in hexane consist of two bands, one with a maximum at 259·5—262·5 mμ (ε 9500—10,280) assigned to a $\pi \longrightarrow \pi^*$ transition, and a second at 405—413 mμ (ε 110—135) assigned to an $n \longrightarrow \pi^*$ transition.

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[7] M. Busch and W. Dietz, *Ber.*, 1914, **47**, 3277.

[8] K. H. Pausacker, *J.*, 1950, 3478.

[9] R. Criegee and G. Lohous, *Chem. Ber.*, 1951, **84**, 219.

[10] O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Analyt. Chem.*, 1951, **23**, 282.

TABLE 2

Ultraviolet maxima (for hexane solutions) of 1-hydroperoxy-1-phenylazoalkanes, $R^1R^2C(OOH){\cdot}N{:}N{\cdot}Ph$[a]

		$\pi \longrightarrow \pi^*$		$n \longrightarrow \pi^*$	
R^1	R^2	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$
Me	Me	266·5	9560	411	134
$-[CH_2]_5-$		268	10,400	413	140
Me	H	267·5[b]	9360	409	124
		267·5[c]	9150	409	125
Pr^n	H	268·5	9260	411	140

[a] Prepared in solution from the corresponding phenylhydrazones (see Experimental section). From α-acetaldehyde phenylhydrazone. [c] From β-acetaldehyde phenylhydrazone.

The spectra of the 1-hydroperoxy-1-phenylazoalkanes in hexane also consisted of two bands, one with a maximum at 266·5—268·5 mμ (ε 9150—10,400), and a second at 409—413 mμ (ε 124—140). Comparison of the spectra of individual 1-hydroperoxy-1-phenylazoalkanes with the corresponding phenylazoalkanes, *e.g.*, 2-hydroperoxy-2-phenylazopropane (IV; $R^1 = R^2 = Me$) with 2-phenylazopropane (II; $R^1 = R^2 = Me$), indicates a shift to longer wavelength in both bands on introducing the hydroperoxide group into the molecule. These shifts correspond to 5·5—6·5 mμ for the $\pi \longrightarrow \pi^*$ band and 2—4 mμ for the $n \longrightarrow \pi^*$. The values of the molar extinction coefficients of both bands remain fairly constant.

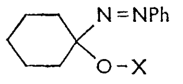
TABLE 3

Ultraviolet maxima (for hexane solutions) of phenylazoalkanes, $R^1R^2R^3C{\cdot}N{:}N{\cdot}Ph$

			$\pi \longrightarrow \pi^*$		$n \longrightarrow \pi^*$	
R^1	R^2	R^3	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$
Me	Me	H	261	9690	408	122
$-[CH_2]_5-$		H	262·5	10,280	410	135
Me	H	H	261	9500	405	127
Pr^n	H	H	262·5	9900	409	124
Me	Me	Me	259·5	10,200	413	110

O'Connor and Rosenbrook[5] reported a difference of 4 mμ in the $n \longrightarrow \pi^*$ band between 2-*p*-tolylazobutane [$\lambda_{max.}$ (MeOH) 402 mμ (ε 174)] and the spectrum of the product obtained on allowing a solution of butanone *p*-tolylhydrazone in heptane to stand during 70 minutes [$\lambda_{max.}$ (heptane) 406 mμ (ε 168)], but this result may be due to a solvent effect.

Degradation work also points to the oxygen function being situated on the carbon atom α to the azo-group. Cleavage of the O–O bond in 1-hydroperoxy-1-phenylazocyclohexane (IV; $R^1R^2 = -[CH_2]_5-$) by treatment with acidified potassium iodide led to the formation of cyclohexanone, and is thought to arise from an intermediate such as (VII). The product resulting from the phenylazo-part of the molecule was not investigated. Intermediates having structures like (VII) are known to break down in an analogous way.[11]



(VII: X = H or I)

Similar results have been obtained by Minisci,[12] who reductively cleaved the O–O bond of 1-hydroperoxy-1-phenylazoalkanes with aqueous solutions of cuprous and ferrous salts, and isolated the corresponding carbonyl compounds. Other workers[13] isolated 1-benzoyl-2-phenylhydrazine on catalytic hydrogenation of the hydroperoxide derived from benzaldehyde phenylhydrazone (IV; $R^1 = Ph$, $R^2 = H$).

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[11] J. T. Edward and S. A. Samad, *Canad. J. Chem.*, 1963, **41**, 1638.
[12] F. Minisci, *Gazzetta*, 1959, **89**, 626.
[13] B. Witkop and H. M. Kissman, *J. Amer. Chem. Soc.*, 1953, **75**, 1975.

Apart from using ultraviolet spectroscopy, O'Connor [1] claimed that the rearrangement of phenylhydrazones to phenylazoalkanes could also be followed by proton magnetic resonance (p.m.r.) spectroscopy. In carbon tetrachloride under nitrogen, the p.m.r. spectrum of cyclohexanone phenylhydrazone was reported to show a gradual decrease of the N–H peak and of the band assigned to the two methylene groups adjacent to C=N. A triplet, characteristic of a hydrogen on a tertiary carbon, also began to appear.

In carbon tetrachloride under nitrogen, we found the p.m.r. spectrum of cyclohexanone phenylhydrazone had absorption at τ 2·70—3·50 (multiplet; 6 protons assigned to the phenyl group and NH), 7·50—8·10 (multiplet; 4 protons assigned to the two methylene groups adjacent to C=N) and 8·10—9·00 (multiplet; 6 protons assigned to the remaining three methylene groups). Contrary to O'Connor's [4] result, the spectrum was unchanged after 7 days at 35°.

The p.m.r. spectrum of phenylazocyclohexane, measured as a neat liquid, had absorption at τ 2·10—2·50 (two multiplets; 5 protons assigned to the phenyl group), 6·32 (quintet; 1 proton assigned to hydrogen on a tertiary carbon) and 8·00—9·00 (multiplet; 10 protons assigned to the five methylene groups).

Recently, Karabatsos and Taller [14] made a thorough investigation of the p.m.r. spectra of phenylhydrazones, and contrary to the findings of O'Connor,[1] were unable to detect any rearrangement of phenylhydrazones to phenylazoalkanes. In an interesting experiment, they passed oxygen through a solution of acetone phenylhydrazone in benzene and observed the change in the p.m.r. spectrum. They found that the doublet at τ 8·16, 8·72, assigned to the *cis*- and *trans*-methyl groups [15] in acetone phenylhydrazone, was replaced by a singlet at τ 8·53, as would be expected for the formation of 2-hydroperoxy-2-phenylazopropane (IV; $R^1 = R^2 =$ Me).

In a similar experiment, we have passed oxygen through a solution of cyclohexanone phenylhydrazone in deuterobenzene. The p.m.r. spectrum of the freshly prepared solution had absorption at τ 2·60—3·40 (multiplet; 6 protons assigned to the phenyl group and NH), 7·75 (multiplet; 2 protons assigned to the *cis*-methylene [15] adjacent to C=N), 8·30 (multiplet; 2 protons assigned to the *trans*-methylene [15] adjacent to C=N), and 8·50—9·00 (multiplet; 6 protons assigned to the remaining three methylene groups). When the oxygen treatment was given, hydroxyl proton absorption appeared at τ 0·27, the phenyl proton absorption divided into two multiplets at τ 2·10—2·50 and 2·60—3·20, similar to the phenyl proton absorption in phenylazocyclohexane, and the cyclohexyl proton absorption merged into a broad multiplet at τ 7·50—9·20. These results are consistent with the formation of 1-hydroperoxy-1-phenylazocyclohexane (IV; $R^1 = R^2 = -[CH_2]_5-$) and characteristically different from those expected for the formation of phenylazocyclohexane. Deuterobenzene rather than carbon tetrachloride was used because of the marked instability of the product in the latter solvent.

We have made several attempts to determine whether small amounts of phenylazoalkanes are formed in conjunction with 1-hydroperoxy-1-phenylazoalkanes during the autoxidation of phenylhydrazones. Chromatography of the crude autoxidation products from cyclohexanone phenylhydrazone on alumina gave no phenylazocyclohexane. To determine if it were possible to isolate small amounts of phenylazocyclohexane in the presence of 1-hydroperoxy-1-phenylazocyclohexane, a mixture of phenylazocyclohexane (10%) and cyclohexanone phenylhydrazone (90%) in hexane was treated with oxygen and the crude product was chromatographed on alumina; the phenylazocyclohexane was quantitatively recovered.

From our results we must conclude that in neutral solution no equilibrium exists between phenylhydrazones and phenylazoalkanes, and we have found no evidence for the rearrangement of phenylhydrazones to phenylazoalkanes as reported by O'Connor.[1] Our

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[14] G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, 1963, **85**, 3624.

[15] See ref. 14 for the assignment of these bands.

results suggest most strongly that the formation of yellow solutions from phenylhydrazones observed by O'Connor was due to autoxidation.

However, our results do not exclude the possibility of tautomeric changes occurring with phenylhydrazones in more polar solvents. Kitaev, Troepol'skaya, and their co-workers[16] have, for several years, been studying the tautomeric behaviour of phenylhydrazones in aqueous methanol using polarographic techniques, and recently Micheel and Dijong[17] reported the establishment of a tautomeric equilibrium between an aldose phenylhydrazone and the corresponding phenylazo-sugar using ether–dioxan and aqueous dioxan. We plan to extend our own work using these and other solvent systems.

The phenylazoalkanes used in this work, except for 2-methyl-2-phenylazopropane, were prepared from the corresponding phenylhydrazones in two steps, in overall yields of 55—70%. The phenylhydrazones were reduced with lithium aluminium hydride in tetrahydrofuran by a modification of the method used by Kratzl and Berger,[18] and the resulting 1-alkyl-2-phenylhydrazines were oxidised with yellow mercuric oxide. A similar method has been used by Renaud and Leitch[19] for the preparation of 1,2-dialkylazo-compounds from dialkylidene azines. This method gave better yields than that of Curtin and Ursprung[20] for the preparation of primary and secondary phenylazoalkanes; their method[20] was used for the preparation of 2-methyl-2-phenylazopropane.

EXPERIMENTAL

Alumina was of type H, 100—200 mesh, supplied by Peter Spence Ltd. Light petroleum refers to the fraction b. p. 40—60°. The identity of compounds was proved where necessary by mixed m. p. and by infrared spectrometry. P.m.r. spectra were determined at 60 Mc./sec. on a Perkin-Elmer R 10 p.m.r. spectrometer using tetramethylsilane as internal reference. Ultraviolet spectra were determined on a Perkin-Elmer 137 u.v. spectrophotometer.

Preparation of Phenylhydrazones.—All phenylhydrazones were prepared according to well-known procedures and were stored under nitrogen. Liquid phenylhydrazones were purified by distillation under reduced pressure and solid phenylhydrazones were purified by recrystallisation.

Acetone phenylhydrazone. This had b. p. 113°/3·5 mm., n_D^{26} 1·585, a very pale yellow liquid which turned bright yellow and then red on exposure to air (lit.,[1] b. p. 108—109°/1·6 mm.).

Cyclohexanone phenylhydrazone. This had m. p. 73·5—76·5° (from aqueous ethanol as white crystals which changed to a red viscous liquid on exposure to air) (lit.,[1] m. p. 74—76°).

n-Butyraldehyde phenylhydrazone. This had b. p. 109—111°/1·5 mm., $n_D^{18\cdot5}$ 1·574, a pale yellow liquid which turned red on exposure to air (lit.,[9] b. p. 167°/24 mm.).

α- and β-Acetaldehyde phenylhydrazone. These compounds were prepared by the method of Laws and Sidgwick.[21] α-Acetaldehyde phenylhydrazone, m. p. 93—100° (from 70% aqueous ethanol containing a trace of sodium hydroxide) formed cream-coloured needles which darkened on exposure to air (lit.,[21] 98°). β-Acetaldehyde phenylhydrazone, m. p. 57—59° (from 70% aqueous ethanol containing a trace of hydrochloric acid) formed cream-coloured needles which darkened on exposure to air (lit.,[21] 56°).

Butan-2-one p-*nitrophenylhydrazone.* This had m. p. 129·5—131·5° (from aqueous ethanol) (lit.,[22] 127°).

Quantitative Oxygenation of Phenylhydrazones.—The uptake of oxygen by phenylhydrazones in several solvents was measured using a micro-gas-uptake apparatus operating at atmospheric pressure. The sample, sufficient to give a total uptake of about 5 ml. of oxygen, was stored in a closed tube inside the apparatus which was flushed with oxygen and allowed to equilibrate. The sample was then allowed to mix with the solvent (20 ml.) and the uptake of oxygen was recorded. Except where stated, the reactions were performed without the addition of a catalyst

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[16] Y. P. Kitaev and T. V. Troepol'skaya, *Bull. Acad. Sci. U.S.S.R.*, 1963, 408, and references therein.

[17] F. Micheel and I. Dijong, *Chem. Ber.*, 1964, **97**, 2409.

[18] K. Kratzl and K. P. Berger, *Monatsh.*, 1958, **89**, 83.

[19] R. Renaud and L. C. Leitch, *Canad. J. Chem.*, 1954, **32**, 545.

[20] D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.*, 1956, **21**, 1221.

[21] E. G. Laws and N. V. Sidgwick, *J.*, 1911, **100**, 2085.

[22] W. Seibert, *Chem. Ber.*, 1947, **80**, 494.

and the solvents used were dried AnalaR grade. The apparatus was only roughly temperature-controlled and all reactions were performed at about 20° under normal lighting conditions (Table 1).

Preparation of Solutions of 1-*Hydroperoxy*-1-*phenylazoalkanes for the Measurement of their Ultraviolet Spectra.*—The phenylhydrazone ($0{\cdot}11$—$0{\cdot}22 \times 10^{-3}$ mole) in spectroscopic grade hexane (10 ml.) was treated with an excess of oxygen and the resulting yellow solution was diluted to concentrations suitable for spectroscopic measurements (Table 2).

Behaviour of Cyclohexanone Phenylhydrazone in Hexane.—(*a*) A solution of cyclohexanone phenylhydrazone (0·32 g.) in dry hexane (100 ml.), on treatment with oxygen until it was bright yellow (30 min.) and evaporation at 20° *in vacuo*, gave a yellow, viscous liquid possessing characteristic infrared bands at $\nu_{\max.}$ (film) 3400s, 875m, 855m, and 830m cm.$^{-1}$. The infrared spectrum indicated that, if phenylazocyclohexane or cyclohexanone phenylhydrazone were present at all, the amounts were very small. The product was unstable and decomposed on standing, with the evolution of gas, but appeared to be fairly stable if left in solution. An attempt to isolate, by chromatography on alumina, any phenylazocyclohexane formed in a similar reaction to that described above was unsuccessful. The same product was obtained if the reaction was performed in carbon tetrachloride.

(*b*) Cyclohexanone phenylhydrazone (0·16 g.) in dry hexane (50 ml.) under nitrogen turned only very pale yellow on standing at 20° for several hours. There was no further development of colour in this solution on heating under reflux during 17 hr.

(*c*) Cyclohexanone phenylhydrazone (0·225 g.) in dry hexane (13 ml.) under nitrogen remained colourless and gave unchanged phenylhydrazone on evaporation after 3 months.

(*d*) Cyclohexanone phenylhydrazone (0·18 g.) in hexane (50 ml.) saturated with water and stored under nitrogen remained colourless. A yellow colour was produced on introducing oxygen and evaporation gave the unstable product obtained previously.

(*e*) In a control reaction, phenylazocyclohexane (0·225 g.) in dry hexane (200 ml.) was treated with oxygen during 2 hr. Evaporation and distillation gave unchanged phenylazocyclohexane (0·185 g., 81%), b. p. 114—115°/3·5 mm., $n_D^{25\cdot5}$ 1·545.

Isolation of Phenylazocyclohexane from a Solution of Phenylazocyclohexane and Cyclohexanone Phenylhydrazone in Hexane.—After cyclohexanone phenylhydrazone (0·903 g.) had been added to phenylazocyclohexane (0·103 g.) in dry hexane (900 ml.), the solution was stirred in the presence of air during 2 hr. and set aside for 16 hr. The yellow solution was evaporated *in vacuo* and the residue was chromatographed on alumina (50 g.). Elution with light petroleum (b. p. 30—50°) gave a crude product which was rechromatographed to give a quantitative recovery of phenylazocyclohexane.

Treatment of 1-*Hydroperoxy*-1-*phenylazocyclohexane with Acidified Potassium Iodide.*—Cyclohexanone phenylhydrazone (5·0 g.) in dry hexane (300 ml.) was treated with oxygen during 1 hr. The resulting yellow solution was stirred at 20° under nitrogen during a further 1 hr. with saturated aqueous potassium iodide (50 ml.) and dilute acetic acid (30 ml.). The mixture was poured into water, the organic layer was separated, and the aqueous layer extracted with ether. The combined organic layers were washed with aqueous sodium thiosulphate and 10% aqueous sodium carbonate and finally dried. Careful evaporation of the solvent gave a liquid (5·5 g.), $\nu_{\max.}$ (film) 1725s cm.$^{-1}$.

The lower-boiling fraction was removed at 50° *in vacuo* and collected in a trap at −80°. Distillation of this fraction gave cyclohexanone (1·3 g., 50%), b. p. 155—175°, identified by its infrared spectrum and 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 160—163° (lit.,[23] 160°).

The higher-boiling fraction was not further investigated but on the basis of its infrared spectrum appeared to contain more cyclohexanone.

Behaviour of Acetone Phenylhydrazone in Hexane.—(*a*) A solution of acetone phenylhydrazone (0·285 g.) in dry hexane (50 ml.), on treatment with oxygen until it was bright yellow (20 min.) and evavoration at 20° *in vacuo*, gave a yellow, viscous liquid possessing characteristic infrared bands at $\nu_{\max.}$ (film) 3400s, 875m, and 850m cm.$^{-1}$. The product was unstable and decomposed with violence after standing for a few minutes.

(*b*) Acetone phenylhydrazone (0·23 g.) in dry hexane (17 ml.) under nitrogen remained colourless and gave unchanged phenylhydrazone on evaporation after 3 months.

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[23] C. F. H. Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955.

(*c*) A 5×10^{-3}M-solution of acetone phenylhydrazone in dry hexane (100 ml.) under nitrogen was treated with phenylhydrazine (2 drops) at 20° during 5 hr. The solution remained colourless.

Reduction of Phenylhydrazones to 1-*Alkyl*-2-*phenylhydrazines* (cf. ref. 18).—The phenylhydrazone (0·2 mole) in dry tetrahydrofuran (50 ml.) was added slowly to a stirred suspension of lithium aluminium hydride (0·4 mole) in dry tetrahydrofuran (150 ml.) at 0° under nitrogen. The mixture was heated under reflux during 6 hr. and set aside for 12 hr. Water (30 ml.) was added cautiously with cooling and stirring, followed by 4N-sodium hydroxide (30 ml.). The mixture was poured into water (1 l.) and the product was isolated with ether. Evaporation of the solvent and fractional distillation gave the pure 1-alkyl-2-phenylhydrazine. All the 1-alkyl-2-phenylhydrazines which were synthesised distilled as colourless liquids but turned yellow on contact with oxygen.

(*a*) 1-*Isopropyl*-2-*phenylhydrazine*. Reduction of acetone phenylhydrazone gave 1-isopropyl-2-phenylhydrazine (80%), b. p. 73—77°/1·0 mm., n_D^{20} 1·542 (lit.,[18] b. p. 118—120°/12 mm., n_D^{20} 1·5468).

(*b*) 1-*Cyclohexyl*-2-*phenylhydrazine*. Reduction of cyclohexanone phenylhydrazone gave 1-cyclohexyl-2-phenylhydrazine (75%), b. p. 111—114°/0·6 mm., n_D^{22} 1·5615 (lit.,[24] b. p. 226°/100 mm.). The product crystallised slowly on standing.

(*c*) 1-*Butyl*-2-*phenylhydrazine*. Reduction of n-butyraldehyde phenylhydrazone gave 1-butyl-2-phenylhydrazine (74%), b. p. 102—107°/1·8 mm., n_D^{23} 1·5345 (Found: C, 73·05; H, 9·7; N, 17·2. Calc. for $C_{10}H_{16}N_2$: C, 73·1; H, 9·8; N, 17·05%) (lit.,[18] b. p. 136—137°/12 mm., n_D^{20} 1·5565).

(*d*) 1-*Ethyl*-2-*phenylhydrazine*. Reduction of acetaldehyde phenylhydrazone (m. p. 72—79°, a mixture of α- and β-isomers) gave 1-ethyl-2-phenylhydrazine (66%), b. p. 81—83°/1·75 mm., $n_D^{24.5}$ 1·5525 (Found: C, 70·4; H, 8·7; N, 20·75. Calc. for $C_8H_{12}N_2$: C, 70·55; H, 8·9; N, 20·55%) (lit.,[18] b. p. 105—107°/12 mm., n_D^{20} 1·5676).

Oxidation of 1-*Alkyl*-2-*phenylhydrazines to Phenylazoalkenes*.—The 1-alkyl-2-phenylhydrazine (0·15 mole) in ether (1 l.) was shaken with yellow mercuric oxide (0·45 mole) under nitrogen during 18 hr. The solid was filtered off and evaporation of the solvent and distillation gave the pure phenylazoalkane. All the phenylazoalkanes which were synthesised were mobile, yellow liquids.

(*a*) 2-*Phenylazopropane*. Oxidation of 1-isopropyl-2-phenylhydrazine gave 2-phenylazopropane (88%), b. p. 31—34°/0·8 mm., $n_D^{21.5}$ 1·520 (lit.,[1] b. p. 75—78°/10 mm., n_D^{20} 1·5252).

(*b*) *Phenylazocyclohexane*. Oxidation of 1-cyclohexyl-2-phenylhydrazine gave phenylazocyclohexane (89%), b. p. 83—87°/0·6 mm., n_D^{22} 1·5485 (lit.,[1] b. p. 106—112°/3 mm., $n_D^{26.5}$ 1·5503).

(*c*) 1-*Phenylazobutane*. Oxidation of 1-butyl-2-phenylhydrazine gave 1-*phenylazobutane* (86%), b. p. 74—81°/2·3—2·8 mm., n_D^{19} 1·522 (Found: C, 74·0; H, 8·6; N, 17·25. $C_{10}H_{14}N_2$ requires C, 74·05; H, 8·7; N, 17·25%).

(*d*) *Phenylazoethane*. Oxidation of 1-ethyl-2-phenylhydrazine gave phenylazoethane (87%), b. p. 52—57°/3·5 mm., $n_D^{20.5}$ 1·534 (lit.,[6] b. p. 82·5—83°/20 mm.).

2-*Methyl*-2-*phenylazopropane*.—This compound was prepared by the method of Curtin and Ursprung[20] (27%), b. p. 57—58°/2 mm., n_D^{27} 1·5095 (lit.,[1] b. p. 61—62°/4·2 mm. n_D^{24-25} 1·5083; lit.,[20] b. p. 50—54°/0·2 mm.).

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[24] R. C. Goodwin and J. R. Bailey, *J. Amer. Chem. Soc.*, 1925, **47**, 167.