to yield 0.43 g. (75%) of crude monomethyl fumarate, m.p. 133–138°. A single recrystallization from ether-hexane afforded 0.37 g. (65%) as white prisms melting at 144–146° (lit., m.p., 144.5°), neutral equivalent 128 (calcd. 130).

By a similar procedure potassium 4,4-dinitro-2-butenamide was converted in 85% yield to fumaric acid, m.p. 214.5–216° dec. (lit., m.p., 217° dec.), neutral equivalent 112 (calcd. 115).

SILVER SPRING, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Tautomerism in Phenylhydrazones[1]

ROD O'CONNOR[2]

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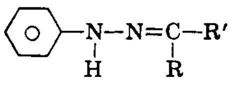
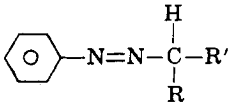
A study of the infrared, visible, ultraviolet, and NMR spectra of a series of phenylhydrazones, methylphenylhydrazones, and benzeneazoalkanes has been made. It is found that freshly prepared phenylhydrazones of aliphatic aldehydes and ketones exist as the hydrazone tautomer. These phenylhydrazones tautomerize rapidly in solution to benzeneazoalkanes. No detectable concentration of the ene-hydrazine tautomer is found in solutions of phenylhydrazones in neutral nonpolar organic solvents.

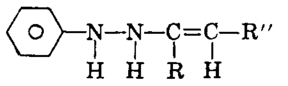
The problem of isomerism of phenylhydrazones among the hydrazone (I), azo (II), and ene-hydrazine (III) forms has been the subject of considerable investigation during the past half century. In addition to the general interest in this tautomerism, with the added potential of *cis-trans* isomers for each tautomer, further interest has been stimulated by the use of phenylhydrazones as analytical derivatives of carbonyl compounds and by considerations of the mechanism of the Fischer indole synthesis, for which phenylhydrazones are starting materials.



I

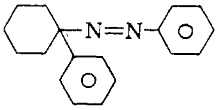


II



III

Tautomerism in phenylhydrazones was first investigated by Freer[3] in 1893. For the next forty years, there was considerable controversy concerning attempts to determine the structures of various phenylhydrazone tautomers and their relative stabilities.[4–8] By the late 1930's it was generally agreed[9] that the hydrazone tautomer was the most stable form and that it was resistant to tautomeric change. In 1947, Grammaticakis[10] recognized a serious flaw in all the earlier work on this problem. There had, as yet, been no study using any one tautomer which might not contain equilibrium amounts of other forms. Grammaticakis prepared the azo compound (IV) to be used as a standard for the ultraviolet and visible spectrum of a benzeneazoalkane. From a comparison of the ultraviolet and visible spectra of phenylhydrazones with that of compound IV, he concluded that phenylhydrazones in solution exist in equilibrium with small quantities of the azo tautomer.[11] He did not report any study of spectra as a function of time and thus failed to establish that equilibrium had been reached (if, indeed, an equilibrium were involved). No serious attempt was made to verify Grammaticakis' conclusions until 1957. At that time, Arbuzov and Kitayev[12] concluded



IV

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[1] The work described in this paper was included in the Ph.D. thesis of the author at the University of California, August, 1958.

[2] National Science Foundation Fellow, 1955–1957, Procter and Gamble Fellow 1957–1958; present address, Montana State College, Bozeman, Mont.

[3] P. C. Free, *J. prakt. Chem.*, **47**, 238 (1893); *Ann.*, **283**, 391 (1894).

[4] E. Fischer, *Ber.*, **29**, 793 (1896).

[5] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

[6] E. C. C. Baly and W. B. Tuck, *J. Chem. Soc.*, **89**, 982 (1906).

[7] K. V. Auwers and H. Wunderling, *Ber.*, **64**, 2748 (1931).

[8] Taku Uemura and Y. Inamura, *Bull. soc. chim. Japan*, **10**, 169 (1935).

[9] P. Ramart-Lucas, J. Hoch, and M. Martynoff, *Pull. soc. chim. France* **4**, 481 (1937).

[10] P. Grammaticakis, *Bull. soc. chim. France*, 438 (1947).

[11] Recently, Grammaticakis' work has been interpreted as evidence for the existence of the ene-hydrazine tautomer [*cf.* K. H. Pausacker and C. I. Schubert, *J. Chem. Soc.*, 1384 (1949), and H. Plieninger, *Ber.*, **83**, 273 (1950)]. Although Grammaticakis did, at one time, believe such a form might exist [*Compt. rend.*, **223**, 804 (1946)], the work in question (ref. 10) showed no evidence of the presence of any ene-hydrazine form in neutral solutions in organic solvents.

[12] A. E. Arbuzov and Y. B. Kitayev, *Doklady Akad. Nauk SSSR*, **113**, 577 (1957).

from a study of polarographic data that (a) aliphatic ketone "phenylhydrazones" were actually ene-hydrazines in the solid state and in fresh solutions; (b) aldehyde and aromatic ketone phenylhydrazones were hydrazones; and (c) tautomerism proceeds in solution from ene-hydrazine to hydrazone to azo forms. Their conclusions are questionable for several reasons. First of all, the use of azobenzene and the phenylhydrazone of benzaldehyde for reference compounds in the polarographic reductions appears unwise. These compounds are fully aromatic and the energy differences between the conjugated —N=N— and its reduced state and the conjugated —C=N— and its reduced state respectively, should be unlike those expected for comparable reductions in the benzeneazoalkanes and phenylhydrazones of aliphatic aldehydes and ketones. Hence, polarographic waves, which are characteristic of these energy differences, should exhibit significant dissimilarities for the fully aromatic and the partly aromatic compounds. In addition, the generalizations made from data obtained using aqueous alcoholic buffer solutions to the solid state and to neutral solutions in organic solvents appear unjustified. The many types of polarographic waves—*e.g.* absorption and kinetic waves—may account for some of their observations.

It was apparent from the confusion concerning the tautomerism of phenylhydrazones that a careful study of the problem was in order.

Approach. As Grammaticakis' azo reference compound (IV) contained an additional phenyl group which might affect the ultraviolet spectrum appreciably, it was decided to use 2-methyl-2-benzenazopropane (method of Curtin and Ursprung[12]) for a standard azo compound incapable of tautomerization. Then 2-benzeneazopropane, benzenazocyclohexane, and 1-benzeneazopentane were prepared by the same method and their structures deduced by comparison of infrared, ultraviolet, visible, and NMR spectra with the standard azo compound.

The methylphenylhydrazones of acetone, cyclohexanone, and heptaldehyde were prepared as standards of the hydrazone form which could not tautomerize to the azo form.

Finally, the phenylhydrazones of acetone, cyclohexanone, and heptaldehyde were prepared and carefully purified. Their infrared, ultraviolet, visible, and NMR spectra were studied in freshly prepared solutions and, as a function of time, in solutions in different solvents.

RESULTS AND DISCUSSION

2-Methyl-2-benzeneazopropane and the other azo compounds used were found to have a characteristic benzeneazoalkane spectrum in the visible and ultraviolet region with λ_{max} at 401–408 mμ, ϵ 125–150, and λ_{max} at 265 mμ, ϵ 7700–10,000 (See Table I). Isolation of solutes by solvent evaporation gave materials of identical refractive indices to the original azo compounds. In the infrared region, all these azo compounds showed the absence of N—H absorption. The N=N bond has been difficult to identify in the infrared, but LeFevre and Werner[13] indicate that an absorption is to be expected in the region of 1400–1450 cm.$^{-1}$ All the azo compounds in this study have several peaks in the region 1400–1500 cm.$^{-1}$, with one of the strongest occurring around 1460 cm.$^{-1}$ It is not certain as yet whether this peak may be, at least partly, due to N=N absorption. The proton magnetic resonance spectra of the azo compounds show in all cases only peaks which can be ascribed to phenyl or to alkyl hydrogens (See Table II).

TABLE I

ULTRAVIOLET AND VISIBLE SPECTRA
(Solvent: 95% ethanol or absolute methanol)

Compound	λ_{max} (mμ)	ϵ (Molar Extinction Coefficient)	λ_{max} (mμ)	ϵ
2-Methyl-2-benzeneazopropane	261	8,400	407	144
Benzeneazocyclohexane	264	10,400	401	156
2-Benzeneazopropane	263	7,700	400	129
1-Benzeneazopentane	263	7,700	401	128
Cyclohexanone phenylhydrazone[a]	275	17,500	—	—
Acetone phenylhydrazone[b]	271	18,000	—	—
Heptaldehyde phenylhydrazone[c]	275	18,000	—	—
α-Form of acetaldehyde phenylhydrazone[d]	270	19,400	—	—
β-Form of acetaldehyde phenylhydrazone[e]	272	18,900	—	—
Cyclohexanone methylphenylhydrazone	252	11,900	290	3420
Acetone methylphenylhydrazone	250	11,800	290	3420
Heptaldehyde methylphenylhydrazone	278	21,100	—	—
Phenylhydrazine	272	7,400	—	—
Unsym-methylphenylhydrazine	247	10,000	283	2800

[a] 6 min. in solution. [b] 9 min. in solution. [c] 5 min. in solution. [d] 12 min. in solution. [e] 13 min. in solution.

All spectra of the azo compounds remain constant with time in solution in neutral organic solvents.[14] This indicates that the azo form is resistant to tautomerism in neutral solution.

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(12) D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.* 21, 1221 (1956).

(13) R. J. W. Le Fevre and R. L. Werner, *Australian J. Chem.* 10, 26 (1957).

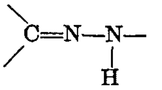
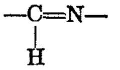
(14) The spectra of the azo compounds do show change on prolonged exposure to fluorescent lighting or sunlight, but this appears to involve *cis-trans* isomerism, as the change is not toward the spectrum of a phenylhydrazone, but is quite similar to that which has been observed under like conditions with azobenzene. See A. Winkel and H. Siebert, *Ber.*, 74, 670 (1941).

TABLE II

NMR SPECTRA[a]

Compound	Type of Hydrogen	Frequency Displacement (in C.P.S. at 40 Mc.)[b]	Relative Peak Areas
2-Methyl-2-benzeneazopropane (in methanol)[c]	Phenyl	−80	5
	$-C(CH_3)_3$	+164	9.1
Benzeneazocyclohexane (in CCl_4)	Phenyl	−80	5
	Cyclic CH_2	+140	9.6
	$-\overset{\vert}{\underset{\vert}{C}}-H$	+96 (triplet)	0.98
2-Benzeneazopropane (in CCl_4)	Phenyl	−80	5
	$>C(CH_3)_2$	+164	6.1
	$-\overset{\vert}{\underset{\vert}{C}}-H$	+100	1.1
1-Benzeneazopentane (in methanol)	Phenyl	−80	5
	n-C_5H_{11} (Not resolved)	*ca.* +160	11
Cyclohexanone methylphenylhydrazone (in CCl_4)	Phenyl	−80	5
	Cyclic CH_2(normal)	+140	6.4
	$-CH_2-\overset{N}{\overset{\Vert}{C}}-CH_2$	+120	4.5
	$N-CH_3$	+92	3.1
Acetone methylphenylhydrazone (in CCl_4)	Phenyl	−80	5
	$CH_3-\overset{N}{\overset{\Vert}{C}}-CH_3$	+124	5.9
	$N-CH_3$	+100	3.2
Heptaldehyde methylphenylhydrazone (in CCl_4)	Phenyl	−80	5
	$n=C_5H_{11}$ (Not resolved)	*ca.* +160	10.5
	$N-CH_3$	+92	3.2
	$N{=}\underset{H(?)^d}{\underset{\vert}{C}}-CH_2-$	+108	3
Cyclohexanone phenylhydrazone (in methanol)	Phenyl	−80	5
	cyclic CH_2(normal)	+140	6.5
	$-CH_2\overset{N}{\overset{\Vert}{C}}-CH_2-$	+120	4.4
	$>C{=}N-\underset{H}{N}-^{e}$	−120	0.8
Acetone phenylhydrazone (in methanol)	Phenyl	−80	5
	$CH_3-\overset{N}{\overset{\Vert}{C}}-CH_3$	+124	5.9
	$>C{=}N-\underset{H}{N}-$	−120	0.8
Heptaldehyde phenylhydrazone (in CCl_4)	Phenyl	−80	5
	$n=C_5H_{11}$	*ca.* +160	11
	$-CH_2-\underset{H(?)}{\underset{\vert}{C}}{=}N$	+108	2.2
	$>C{=}N-\underset{H}{\underset{\vert}{N}}-$	−120	0.4
α-Form[f] of acetaldehyde phenyl (in methanol)	Phenyl	−80	5
	CH_3	+148	3.3
	$>C{=}N-\underset{H}{\underset{\vert}{N}}-$	−96	1.15
	$-\underset{H}{\underset{\vert}{C}}{=}N-$	(?)[g]	—

TABLE II (*Continued*)

Compound	Type of Hydrogen	Frequency Displacement (in C.P.S. at 40 Mc.)[b]	Relative Peak Areas
β-Form of acetaldehyde phenylhydrazone (in methanol)	Phenyl	−80	5
	CH_3	+160	2.7
	 $>C{=}N{-}N(H){-}$	−100	0.8
	 $-C(H){=}N-$	(?)	—

[a] Spectra were obtained by use of a high-resolution, NMR spectrometer and associated magnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at approximately 10,000 gauss. Spectra were calibrated in terms of displacement in cycles per second (cps) from the proton resonance of water. Negative frequency displacements indicate resonances occurring at lower field relative to the reference. [b] Assignments of frequency displacements to a given type of hydrogen are consistent with the best tabulated data [Varian Associates, *Radio-Frequency Spectroscopy*, Vol. 1, No. 2 (April, 1954), pamphlet and N. F. Chamberlain, *Anal. Chem.*, 31, 56 (1959)]. [c] Spectra which were taken of methanol solutions were also run in carbon tetrachloride to show that methanol —CH_3 and —OH peaks did not interfere. [d] This type of proton is not expected to appear in the region shown and may actually be obscured by the phenyl hydrogen peak instead. [e] The assignment of the small peak near −120 c.p.s. to the hydrogen on nitrogen was made on the following basis: 1) It was present in the spectra of all compounds of this study having an N—H band in the infrared and was absent when that band was missing. 2) It was present in the spectra of all aldehyde and ketone phenylhydrazones and absent from the spectra of the azo compounds. 3) It was absent from the spectra of all the *N*-methylphenylhydrazones and was replaced therein by a peak near +100 cps assigned to *N*-methyl hydrogens, although the rest of the spectra of corresponding phenylhydrazones and methylphenylhydrazones were essentially identical. 4) It was found in the spectra of both α- and β-acetaldehyde phenylhydrazones, which are shown to be geometrical isomers of the hydrazone form. The assignment does not correspond to that of Arison *et al.* [See Arison, Erickson, Trenner, and Schoenewaldt, *Chem. & Ind.*, 1627 (1958)], but their reported values of −265 c.p.s. and −313 c.p.s. are for N—H protons when involved in hydrogen bonding with oxygen. [f] The α-form of acetaldehyde phenylhydrazone has been designated as that melting around 100°, while the form melting near 57° is designated as β-. [See: E. G. Laws and N. V. Sidgwick, *J. Chem. Soc.*, 99, 2085 (1911)]. [g] No isolated peak was observed which could be ascribed to the aldehyde type hydrogen. It seems possible that this peak may not have been resolved from the phenyl peak since it was expected to appear in that region (*cf.* footnote *b*).

The methylphenylhydrazone of heptaldehyde shows in the ultraviolet region a λ_{max} at 278 mμ, ε 21,100, whereas the methylphenylhydrazones of the aliphatic ketones show two peaks, λ_{max} at 250–252 mμ, ε 12,000, and λ_{max} at 290 mμ, ε 3420. These differences do not appear to involve tautomeric forms, but are similar in nature to the difference between the spectrum of phenylhydrazine and *unsym*methylphenylhydrazine (see Table I). In the infrared region, the absence of N—H absorption in the 3100–3300-cm.$^{-1}$ range is noted. The C=N absorption is believed to appear in the vicinity of 1640 cm.$^{-1}$ [15] This is difficult to resolve from the strong phenyl peak at 1600 cm.$^{-1}$, but all the methylphenylhydrazones do show a shoulder around 1640 cm.$^{-1}$ on the phenyl peak. The NMR spectra of the methylphenylhydrazones show nothing characteristic of hydrogen on nitrogen (see Table II). From these data, it can be concluded that the methylphenylhydrazones exist as the hydrazone tautomer, with no detectable amounts of ene-hydrazine present. The latter would have been manifested by an N-H peak in the infrared or NMR spectra.

The isomeric α- and β-forms of acetaldehyde phenylhydrazone were given particular attention as they were at one time believed to be ene-hydrazine and hydrazone tautomers[3] and later were considered geometrical isomers of the hydrazone form.[16] No definite evidence of their structures was yet available when this study was initiated. It was found that freshly prepared solutions of the two forms had nearly identical ultraviolet spectra (see Table I) and that these spectra were definitely not those of benzeneazoalkanes. The NMR spectra (see Table II) were also very similar. In their infrared spectra (10% carbon tetrachloride solutions) both isomers exhibited N—H absorption at 3300 cm.$^{-1}$ and the shoulder at 1640 cm.$^{-1}$ found in the methylphenylhydrazone spectra. The infrared spectra of the two forms were superimposable except that the α-form showed splitting in the band at 2900 cm.$^{-1}$ and very weak peaks at 1218 cm.$^{-1}$ and 655 cm.$^{-1}$ which were absent in the spectrum of the β-form. Isolation of solutes by solvent evaporation permitted recovery of solids with the original melting points. The two isomers underwent tautomerization to the benzeneazoalkane structures at significantly different rates (α-form approximately twice as fast as β-form) when hexane solutions were allowed to stand. From the striking similarity of all the spectra of the two isomers, it must be concluded that they are not tautomers, but geometrical isomers. The spectra are obviously not those of benzeneazoalkanes and the ene-hydrazine form (V) has no possibility of geometrical isomerism. Thus, these isomers can

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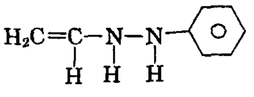
(15) E. M. Tanner, *Spectrochim. Acta*, 20 (1959).

(16) K. A. Jensen and B. Bak, *J. prakt. Chem.*, 151, 167 (1938).



V

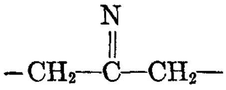
only be geometrical isomers of the hydrazone tautomer and, hence, good reference compounds for the ultraviolet spectrum of a hydrazone form.

It was now established, by the study of the spectra of the α- and β-forms of acetaldehyde phenylhydrazone, that the ultraviolet spectrum of a hydrazone tautomer should show a λ_{max} around 270 mμ, ϵ around 18,000, and have no detectable absorption in the vicinity of 400–420 mμ. The NMR spectrum of a hydrazone tautomer should contain evidence of phenyl, alkyl, and N—H type protons.

A study of the ultraviolet and NMR spectra of freshly prepared solutions of cyclohexanone phenylhydrazone, acetone phenylhydrazone, and heptaldehyde phenylhydrazone revealed the peaks expected of a hydrazone tautomer (see Tables I and II). The infrared spectra were consistent with this structural assignment, all spectra containing N—H bands in the 3300–3450-cm.$^{-1}$ range and being otherwise nearly identical with the spectra of the corresponding methylphenylhydrazones. Isolation of solutes from fresh solutions by solvent evaporation gave compounds identical to the original solutes. Thus it is apparent that freshly prepared phenylhydrazones of aliphatic aldehydes and ketones do exist as the hydrazone form.

It was noted that on standing, solutions of phenylhydrazones began to turn yellow and the spectra of these solutions began to approach those of the corresponding benzeneazoalkanes. For example, the ultraviolet and visible spectrum of cyclohexanone phenylhydrazone in hexane became identical with that of benzeneazocyclohexane in seven minutes at a concentration of $6 \times 10^{-3}M$. Isolation of the isomerization product by solvent evaporation followed by vacuum distillation gave a single compound, identical in refractive index with authentic benzeneazocyclohexane. In carbon tetrachloride, the same change occurred in thirty minutes at a concentration of $4 \times 10^{-3}M$. The rate of tautomerization decreased greatly when methanol was used as a solvent, only 30% tautomerization occurring in twenty minutes and 60% by the end of five hundred minutes. After fifty minutes it became apparent from a study of the visible and ultraviolet spectra that some side reaction was involved in methanol solution, as the ultraviolet peak at 275 mμ was disappearing much more rapidly than was warranted by the rate of appearance of the azo peak around 410 mμ. In aqueous methanol (50% water), tautomerization was almost completely replaced by the unknown side reaction, which may possibly involve formation of the ene-hydrazine tautomer. The nature of this side reaction has not yet been investigated.

The phenylhydrazones of aldehydes show a slower rate of tautomerism than do those of the ketones studied. Heptaldehyde phenylhydrazone requires forty minutes for complete conversion to the azo form in $6 \times 10^{-3}M$ hexane solution.

The course of the tautomerism can also be followed with the NMR spectra. In the case of the phenylhydrazone of cyclohexanone, the NMR spectrum of a carbon tetrachloride solution shows a gradual decrease of the N—H peak at -120 cps and of the band at $+120$ cps assigned to the  $-CH_2-\overset{\overset{\displaystyle N}{\|}}{C}-CH_2-$ protons (see Table II), while the triplet at $+96$ cps characteristic of hydrogen on a tertiary carbon begins to appear and the cyclic CH_2 band at $+140$ cps shows a corresponding increase.

As the spectra of the benzeneazoalkanes remains constant with time in solution, it would appear that the tautomerism of phenylhydrazones of aliphatic aldehydes and ketones to the corresponding benzeneazoalkanes is either an irreversible reaction in neutral solution or that any equilibrium involved must be almost entirely in favor of the azo tautomer.

CONCLUSION

It has been shown that phenylhydrazones of aliphatic ketones and aldehydes originally exist as the hydrazone tautomer. The conversion of the hydrazone form to the more stable azo tautomer is rapid in solution. Thus it is apparent that reported spectra of phenylhydrazones must be accompanied by a statement of time in solution and of solvent used. No evidence has been found for the existence of the ene-hydrazine tautomer in neutral solutions of phenylhydrazones in nonpolar solvents, although the possibility of its occurrence in solutions in polar solvents has not been ruled out.

EXPERIMENTAL

NMR spectra. The spectra were obtained using a Varian High Resolution NMR spectrometer (Varian Associates, Palo Alto, Calif.) operating at a frequency of 40 mc. and a field strength of about 10,000 gauss. The magnet was equipped with a super-stabilizer system and associated slow sweep unit to improve stability and resolution. Samples were contained in 3-mm. O.D. glass tubes, sealed under nitrogen, and spun at 600–900 r.p.m. to average out horizontal field gradients.

The solutions used were saturated (30–60% by weight of solute) using carbon tetrachloride or methanol as solvent. All solutions were stored in Dry Ice until immediately before use, when they were allowed to reach room temperature (22–27°) just before the spectra were recorded.

Infrared spectra. All infrared spectra were taken on a Baird recording double-beam spectrophotometer using freshly prepared 10–20% solutions in carbon tetrachloride.

Ultraviolet and visible spectra. The spectra were taken using a Cary model 14 recording spectrophotometer. Solutions used were about $5 \times 10^{-5} M$ for ultraviolet and about $5 \times 10^{-3} M$ for visible spectra. Optical density was kept in the range 0.2–1.5. For initial comparison spectra, all solutions were absolute methanol or 95% ethanol. For spectra of all phenylhydrazones, the time in solution was noted at the point when the λ_{max} was reached.

2-Methyl-2-benzeneazopropane. This reference compound was prepared by the method of Curtin and Ursprung[12] from *t*-butylzinc chloride and benzenediazonium fluoborate in 35% yield. Purification was by steam distillation followed by fractionation through a 1-m. Podbielniak column, b.p. 61–62°/4.2–4.5 mm. (Reported[12] b.p. 52–53°/0.2 mm.) n_D^{24-25} 1.5083; $n_D^{20.7}$ 1.5103.

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.1; H, 8.6; N, 17.3. Found: C, 74.1; H, 8.9; N, 17.2.

Benzeneazocyclohexane.[17] Cyclohexylmagnesium chloride was prepared by the method of Gilman and Catlin[18] and was converted to the zinc reagent and allowed to react with benzenediazonium fluoborate in the same manner as in the *t*-butyl case above. The product was steam distilled and then fractionated using a 0.7-m. Vigreux column. The total yield of purified benzeneazocyclohexane was 14%, b.p. 106–112°/3 mm.; $n_D^{26.5}$ 1.5503.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.6; H, 8.56; N, 14.88. Found: C, 76.9; H, 8.49; N, 14.97.

2-Benzeneazopropane. This material was prepared from isopropylzinc chloride and benzenediazonium fluoborate in the usual manner. The product was steam distilled and fractionated through a 1-m. Pobielniak column, yield 10%; b.p. 75–78°/10 mm. (reported b.p.[17] 110°/28 mm.) $n_D^{20.0}$ 1.5252 (reported[17] 1.5249).

Anal. Calcd. for $C_9H_{12}N_2$: C, 73.0; H, 8.1; N, 18.9. Found: C, 72.9; H, 7.0; N, 18.3.

1-Benzeneazopentane. The *n*-pentylmagnesium chloride used was prepared by the method of Huston and Langham[19] and was allowed to react with zinc chloride and then with the diazonium salt in the usual way. Purification by steam distillation followed by Podbielniak fractionation gave a yield of 8%; b.p. 120–125°/30 mm.; $n_D^{20.5}$ 1.5115.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 75.0; H, 9.09; N, 15.9. Found: C, 75.4; H, 9.03; N, 15.6.

Cyclohexanone phenylhydrazone. Freshly distilled cyclohexanone and redistilled phenylhydrazine were mixed in equimolar amounts in an Erlenmeyer flask. Vigorous shaking for 10 min. produced much heat and a solid product. Crystallization and recrystallization from aqueous ethanol produced white needles, yield 85%; m.p. 74–76° (evac. cap.) (reported[20] m.p., 74–77°).

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.6; H, 8.56; N, 14.88. Found: C, 77.0; H, 8.60; N, 14.50.

Cyclohexanone methylphenylhydrazone. This product was obtained from cyclohexanone and *unsym*-methylphenylhydrazine in the same manner as the phenylhydrazone; yield 85%. Purification of the oil was by distillation through a 1-m. Podbielniak column; b.p. 126–127°/1.7 mm.; $n_D^{20.0}$ 1.5703.

Anal. Calcd. for $C_{13}H_{18}N_2$: C, 77.2; H, 8.9; N, 13.9. Found: C, 77.3; H, 8.9; N, 13.7.

Acetone phenylhydrazone. Purified acetone in slight excess was treated with phenylhydrazine in a Claisen flask, the mixture shaken for 15 min., then distilled, b.p. 108–109°/1.6 mm. (reported b.p., 140°/16 mm.[21]; 161°/54 mm.[22]); yield 90%. The product slowly crystallized to off-white crystals, m.p. 27-29° (reported,[6] m.p. 26.6°).

Anal. Calcd. for $C_9H_{12}N_2$: C, 73.0; H, 8.1; N, 18.9. Found: C, 72.4; H, 8.47; N, 18.7.

Acetone methylphenylhydrazone. Prepared from *unsym*-methylphenylhydrazine and acetone in the manner used to obtain the phenylhydrazone, yield 85%; b.p. 94–102°/9 mm. (reported b.p.[23] 215–216° dec.; 182°/200 mm.); $n_D^{20.0}$ 1.5582.

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.1; H, 8.6; N, 17.3. Found: C, 73.7; H, 8.7; N, 17.0.

Heptaldehyde phenylhydrazone. Because heptaldehyde is difficult to store, the material used was purified by distillation at reduced pressure into a receiver containing a small amount of hydroquinone. This product was stable for long periods of time when stored under nitrogen, over 2% hydroquinone, in the refrigerator. The pure aldehyde boiled at 68.5–69.5°/42 mm.

The phenylhydrazone was prepared in the manner used to obtain acetone phenylhydrazone. After distillation, the product was washed with 10% sodium hydroxide to remove residual hydroquinone. The hydrazone was dried and distilled through a 0.7-m. Vigreux column, yield 80%; b.p. 119–119.5°/0.15 mm. (reported b.p. 202.5–203°/19. mm.[24]; 240°/77 mm.[25]); $n_D^{20.0}$ 1.5474.

Anal. Calcd. for $C_{13}H_{20}N_2$: C, 76.5; H, 9.81; N, 13.7. Found: C, 76.8; H, 9.82; N, 13.5.

Heptaldehyde methylphenylhydrazone. This material was prepared and purified in the same manner as the phenylhydrazone; yield 90%; b.p. 174–180°/14 mm. (reported[26] b.p. 169–172°/5 mm.); $n_D^{20.0}$ 1.5467.

Anal. Calcd. for $C_{14}H_{22}N_2$: C, 77.2; H, 10.1; N, 12.8. Found: C, 77.2; H, 10.49; N, 12.6.

α-Form of acetaldehyde phenylhydrazone. The preparation of this product was by the standard literature method.[27,28] It was recrystallized three times from 75% ethanol containing a trace of sodium hydroxide; yield 70%; m.p. 97.5–99.5° (reported m.p. 98–101°[12]; 98°[27]; 99–100°[16]; 98–101°[28]).

Anal. Calcd. for $C_8H_{10}N_2$: C, 71.6; H, 7.46; N, 20.9. Found: C, 71.6; H, 7.44; N, 20.8.

β-Form of acetaldehyde phenylhydrazone. The preparation of this form has also been previously reported.[27,28] Recrystallization from 75% ethanol containing a trace of hydrochloric acid gave; 85% yield; m.p. 58–59° (reported m.p. 57°[12,16] 56°[27]; 51–57°[28]).

Anal. Calcd. for $C_8H_{10}N_2$: C, 71.6; H, 7.46; N, 20.9. Found: C, 71.9; H, 7.51: N, 20.7.

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