confirming its identity as 2-chloro-4-chloromethylglutaronitrile. The yield of this addition was quantitative.

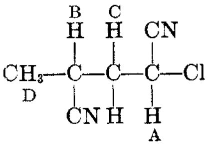
2-Chloro-4-methylglutaronitrile (V).—To a 500-ml Parr bottle was charged 14 g (0.1 mole) of IV dissolved in 100 ml of methanol. To this was added 1.0 g of 5% Pd–C and the bottle was attached to the Parr hydrogenator. The reaction proceeded rapidly at 40 psi and 50° and was essentially complete in 5 min. The reaction mixture was filtered to remove catalyst and distilled under reduced pressure to yield a clean colorless oil, bp 93–95° (0.5 mm).

Anal. Calcd: Cl, 24.61; N, 19.75. Found: Cl, 25.01; N, 20.72.

The nmr spectrum can be interpreted as shown in Table IV. From the chemical shift, D is a methyl group. From its splitting ($J = 7$ cps, doublet) it is attached to a carbon bearing only one hydrogen. For a very simple compound we would seek to find the proton split into a quartet by the methyl group. As a first approximation, this would appear to be given by the protons, B (an approximation only in that these protons are coupled to protons on another adjacent carbon, consequently, the multiplicity observed). From an examination of the neat spectrum, A is trying to be a triplet. It is probably safe to assume then that A is due to a proton adjacent to two other protons which are not equivalent. For these reasons, we feel the structure is (essentially) as shown below.

TABLE IV

Peak	Approximate chemical shift, τ	Area	Relative area
A	5.7	3.4	1.0 (1)
B	7.6	4	1.18 (1)
C	8.2	77.6	2.24 (2)
D	9.5	9.5	2.8 (3)

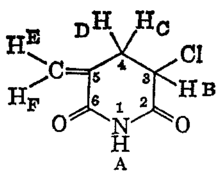


$$\underset{\text{D}}{\mathrm{CH_3}}-\overset{\overset{\text{B}}{\text{H}}}{\underset{\text{CN}}{\text{C}}}-\overset{\overset{\text{C}}{\text{H}}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CN}}{\underset{\underset{\text{A}}{\text{H}}}{\text{C}}}-\text{Cl}$$

3-Chloro-5-(*exo*-methylene)glutarimide (VI).—To a 100-ml three-neck flask fitted with dropping funnel, drying tube, and magnetic stirrer was charged 25 g of concentrated sulfuric acid (85%). To this was added 14 g (0.1 mole) of IV over a 90-min period. The solution was stirred 4 hr and poured into 50 g of ice–water. The acidic solution was stripped to half its volume under reduced pressure; the precipitated solid was filtered and air dried. Recrystallization from methanol gave 5 g (30%) of light yellow powder, mp 141–142°.

Anal. Calcd for $C_6H_6ClNO_2$: C, 45.00; H, 3.87, Cl, 22.25; N, 8.78. Found: C, 44.91; H, 3.89; Cl, 22.24; N, 8.60.

The nmr spectrum of the structure



should give the area under the peaks due to $\mathrm{H_B}$:($\mathrm{H_C} + \mathrm{H_D}$):$\mathrm{H_E} = \mathrm{H_F}$ as 1:2:1:1. The area found was as 1.1:2.0:0.9:1.1. $\mathrm{H_A}$ would be expected to be a singlet, which it is. Usually amino hydrogens give rise to broad peaks due to the effect of the nitrogen quadruple moment on the spin-lattice relaxation time. However, cases are known where the H in -CONH- groups gives rise to sharp singlets[7] as was observed here. Carbon 3 is asymmetric. Inspection of models show that $\mathrm{H_B}$ is slightly different (as far as magnetic environment is concerned) depending on which optical isomer, *d* or *l*, we inspect. Assuming that equal quantities of both are present, we would expect to see two very closely spaced triplets because of spin–spin coupling with $\mathrm{H_C}$ and $\mathrm{H_D}$. Indeed, a gross triplet with signs of this extra complexity is noted in the spectrum. The spectrum of VI in CF_3CO_2D also shows a clear resonance at τ 5.24 as expected. $\mathrm{H_C}$ and $\mathrm{H_D}$ if equivalent would exist as a doublet due to spin–spin coupling with $\mathrm{H_B}$. They are not equivalent though and each splits the other as well as being coupled to $\mathrm{H_B}$. A complex peak attributed to this interaction is found at τ 5.78. $\mathrm{H_E}$ and $\mathrm{H_F}$ are not equivalent and hence should exist as small peaks which should each be split into doublets with small coupling constants. This was found at τ 3.98 and 3.33. Over-all, the predicted and observed nmr spectra are in excellent agreement.

Sodium Bisulfite Addition Product of 2-Chloro-4-(methylene)-glutaronitrile (VII).—To a 250-ml one-neck flask fitted with magnetic stirrer and heating mantle were charged 14 g (0.1 mole) of IV and 11.4 g (0.11 mole) of sodium bisulfite in 100 ml of water. The mixture was stirred and heated to its reflux temperature. Reflux was maintained for 3 hr. The solution was then cooled and the white, crystalline bisulfite addition product was separated by filtration. The bisulfite addition product was recrystallized from water and dried at reduced pressure to yield 24.0 g (97%), mp 235–236°, of white crystalline product.

Acknowledgment.—The authors wish to express their appreciation to Dr. D. P. Wyman for his aid in the interpretation of our nmr spectra.

[7] G. V. D. Tiers and F. A. Bovey, *J. Phys. Chem.*, **63**, 302 (1959).

The Synthesis and Thermal Rearrangement of Substituted α,α-Diphenyl-N-benzhydrylnitrones

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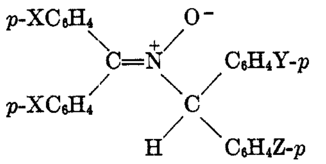
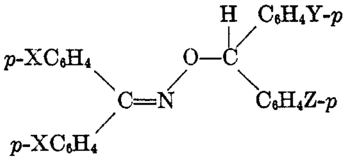
The synthesis of several substituted α,α-diphenyl-N-benzhydrylnitrones is described. A comparison of synthetic methods involving either alkylation of benzophenone oxime anions with benzhydryl halides or the condensation of diaryl ketimines with N-benzhydrylhydroxylamine is presented. The nitrones were thermally isomerized to the corresponding oxime O-ethers.

A previous investigation of α,α-diphenyl-N-benzhydrylnitrone (Ia) revealed that this compound undergoes a nearly quantitative thermal rearrangement to benzophenone O-benzhydryloxime (IIa).[1] Limited evidence was presented in support of a concerted rearrangement involving a quasi-three-membered ring transition state. However, the evidence did not exclude the possibility of initial carbon–nitrogen bond breaking leading to a benzhydryl cation and an oxime anion followed by collapse to products. The present work was directed toward the preparation of a number of substituted α,α-diphenyl-N-benzhydrylnitrones (I) suitable for a detailed kinetic probe of this reaction. Authentic samples of the rearrangement products (II) were also required.

[1] A. C. Cope and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **72**, 4896 (1950).

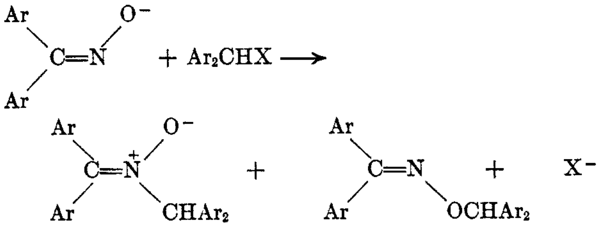


Ia, $X = Y = Z = H$
b, $X = Y = H$; $Z = CH_3$
c, $X = CH_3$; $Y = Z = H$
d, $X = Cl$; $Y = Z = H$

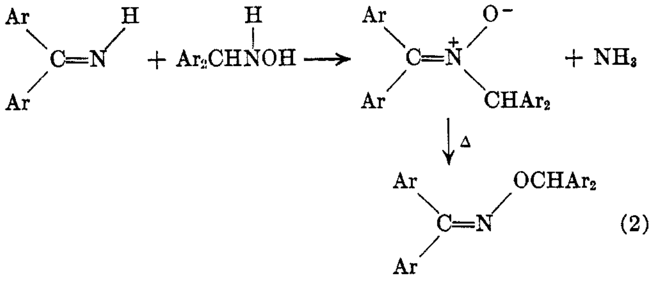


IIa, $X = Y = Z = H$
b, $X = Y = H$; $Z = CH_3$
c, $X = CH_3$; $Y = Z = H$
d, $X = Cl$; $Y = Z = H$

Several routes to the desired nitrones were considered.[2] Of these, two were selected for use in the present study. They are (a) the alkylation of diaryl ketoxime anions with benzhydryl halides (eq 1) and (b) the condensation of substituted benzhydrylidenimines with N-benzhydrylhydroxylamine (eq 2).

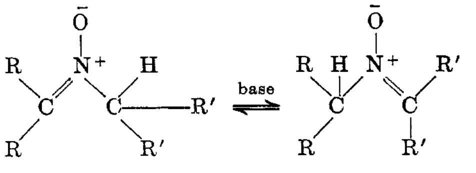


(1)



(2)

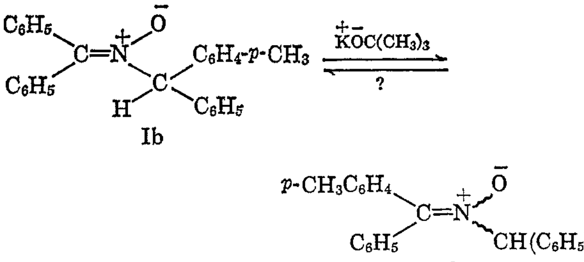
The first method suffers from problems inherent in heterogeneous reactions.[3] The alkylations frequently fail to go to completion. Thus the nitrones are not only contaminated by oxime O-ethers by way of an ambident alkylation, but also by unreacted starting materials.[1,3] A further complication arises in the presence of strong bases (used to generate the oxime anion) where nitrones sometimes undergo tautomerization[1,3,4] (eq 3). The second synthetic approach (eq 2) which has not previously been reported for diaryl ketimines and benzhydryl hydroxylamines is limited by the fact that at temperatures required for the condensation, the rate of rearrangement of the nitrone product to the corresponding oxime O-ether becomes measurable. In the present work this difficulty was circumvented by careful control of reaction temperatures and times.



(3)

Results and Discussion

Nitrone Ia has been prepared by the alkylation of benzophenone oxime with benzhydryl bromide in yields of 16 and 31%.[1] In the present work, Ib was obtained in 7% yield by the alkylation procedure. The ultraviolet spectrum is nearly identical with that for Ia, showing a characteristic nitrone absorption at 310 mμ usually identified as the K band.[5] In this alkylation molar equivalents of potassium *t*-butoxide and benzophenone oxime were employed to generate the oxime anion. The possibility that a small excess of this strong base remained in the presence of the nitrone during the alkylation raises the question as to actual location of the methyl group in the product. A Behrend-type tautomerization could lead to an isomeric mixture of three different nitrones (eq 4). A comparison of the nmr spectra of Ia, b, and c provides an indication, but not convincing evidence, that the structure of Ib is correctly represented. Thus the benzhydryl tertiary proton of Ib appears at 6.24 ppm relative to tetramethylsilane, whereas in both Ia and Ic (both bearing unsubstituted benzhydryl groups) the tertiary proton absorbs at 6.30 ppm. However, although the methyl proton absorption in Ib (2.34 ppm) falls between the two methyl singlets in Ic (2.32 and 2.43 ppm), its position is very close to the lower field methyl peak. To substantiate further the structure of Ib a sample was subjected to acid hydrolysis. The neutral fraction from this hydrolysis was treated with 2,4-dinitrophenylhydrazine, and the 2,4-dinitrophenylhydrazone of benzophenone was isolated in 78% yield. After benzophenone 2,4-dinitrophenylhydrazone and small amounts of the starting reagent were separated, the residue was treated with α-naphthyl isocyanate in an attempt to isolate *p*-methylbenzhydrol as its α-naphthylurethan. No such derivative formed. This result is consistent with the observations of Wragg and Stevens[6] who found that N-diphenylmethylhydroxylamine when hydrolyzed in concentrated hydrochloric acid forms bis(diphenylmethyl) ether. The probable course of the hydrolysis of Ib is then shown in eq 5.



(4)

cis and *trans*

Cope[1] has shown that IIa can be obtained in high yield from Ia by heating the nitrone to 200° in the absence of solvent. Consequently a sample of Ib was

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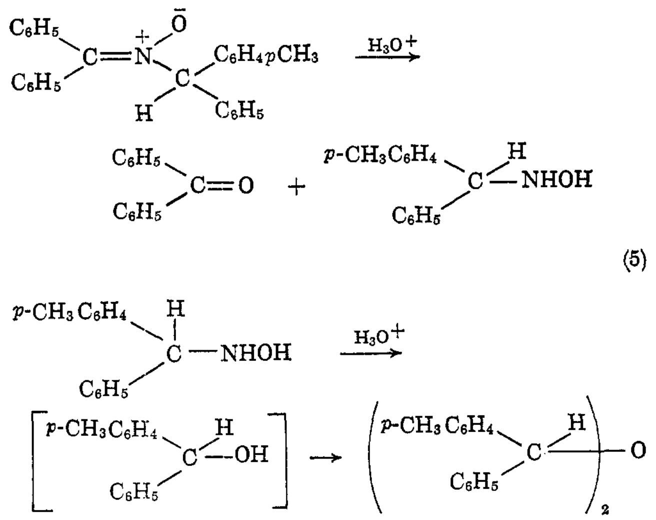
[2] See J. Hamer and A. Macaluso, *Chem. Rev.*, **64**, 473 (1964), for a recent review of nitrones and general methods of synthesis.

[3] See P. A. S. Smith and J. E. Robertson, *J. Am. Chem. Soc.*, **84**, 1197 (1962), for a discussion of factors influencing alkylation of oxime salts.

[4] R. Behrend, *Ann.*, **265**, 238 (1891); C. Neubauer, *ibid.*, **298**, 187 (1897).

[5] See ref 2, p 475.

[6] A. H. Wragg and T. S. Stevens, *J. Chem. Soc.*, 461 (1959).



(5)

sealed in an evacuated glass tube and heated at 200° for 35 min. The product (IIb) crystallized from a petroleum ether–ether mixture in 82% yield. The ultraviolet spectrum of IIb is nearly identical with that for IIa (see Experimental Section), but markedly different from the ultraviolet spectrum of IIc. This not only provides evidence for the structure assigned to IIb, but serves to confirm the structure of Ib from which it is derived.

While investigating the alkylation of benzophenone oxime with benzhydryl bromide Cope[1] observed that the solvent benzene (in which the oxime anion is only slightly soluble) could be replaced by *t*-butyl alcohol apparently without serious loss of the halide by reaction with the solvent. Although this change permits a homogeneous alkylation, the nitrone/oxime O-ether yield ratio dropped from 1/1.7 to 1/3.0. In the present study, after an unsuccessful attempt to prepare Ic by alkylating 4,4′-dimethylbenzophenone oxime with benzhydryl bromide in benzene, the alkylation was carried out in *t*-butyl alcohol. However, from the reaction mixture only the corresponding oxime O-ether (IIc) and unreacted oxime could be isolated. This oxime O-ether was shown to be identical with the O-ether obtained by thermal isomerization of Ic which had been prepared using the ketimine–N-benzhydrylhydroxylamine condensation (see below).

Because of the disadvantages associated with the nitrone synthesis employing alkylation of oxime anions it seemed desirable to explore the possibilities of imine–hydroxylamine condensations (eq 2). The report[1] that only O-triphenylmethylbenzaldoxime could be isolated from the related condensation of benzaldehyde and N-triphenylmethylhydroxylamine cast some doubt upon the possibility of the proposed synthesis. The benzaldehyde condensation must lead to α-phenyl-N-triphenylmethylnitrone, but under the conditions of the reaction (130°) the nitrone apparently rapidly rearranges to the oxime O-ether. This pointed out the need for careful control of the reaction temperatures and times if nitrones were to be isolated.

After extensive exploration, these conditions were established. Using this method, nitrones Ia, c, and d were prepared in fair to good yields. In each case the isolation of pure nitrone was very much easier than encountered in the alkylation reactions. N-Benzhydrylhydroxylamine needed for the syntheses was obtained by the method of Exner.[7] This involved the hydrolysis of α,α-dimethyl-N-benzhydrylnitrone prepared from acetoxime and benzhydrylbromide. For use in the synthesis of Ia, benzhydrylidenimine hydrochloride was obtained from the reaction of ethyl carbamate with dichlorodiphenylmethane.[8] The requisite imines employed in the preparation of Ic and Id were made by the reactions of appropriate aryl Grignard reagents and aryl cyanides according to the procedure of Pickard and Vaughan.[9] The diarylketimine–benzhydrylhydroxylamine condensations were carried out by heating a concentrated solution of the two reactants in boiling (90–100°) petroleum ether for 12–24 hr. In the preparation of Ia, the free imine was liberated in solution from its hydrochloride using ammonia. After the completion of the reaction period (and separating ammonium chloride where necessary), the cooled petroleum ether solutions deposited the nitrones in fair purity. Recrystallization of the nitrones from heptane gave the pure products. In this way the unsubstituted nitrone Ia was obtained in 45% yield. Nitrones Ic and Id were similarly prepared in yields of 62 and 39%, respectively.

The oxime O-ethers IIc and IId were obtained by the thermal isomerization of the corresponding nitrones as discussed previously for IIb.

In any attempt to evaluate the scope of the ketimine–N-alkyl- (or aryl-) hydroxylamine condensation it is clear that potential steric interaction of *cis*-oriented groups attached to nitrogen and the α-carbon of nitrones will provide a major limitation to this method. Such interactions have been recognized as important in influencing the electronic spectra of nitrones.[10] As the size of the interacting groups (originally attached to the imine and substituted hydroxylamine) increase, the temperatures required for the condensation increase. However, at the elevated temperatures rearrangement of the initially formed nitrones to the corresponding oxime O-ethers becomes a serious "side reaction." Thus Cope and Haven[1] were able to isolate only benzophenone O-triphenylmethyloxime from the condensation of benzhydrylidenimine and N-triphenylmethylhydroxylamine at 120°. They assumed that the nitrone was an intermediate which rapidly rearranged. Again, the condensation of benzaldehyde with N-triphenylmethylhydroxylamine at 130° led to O-triphenylmethylbenzaldoxime as the only isolable product.[1] The nitrone is undoubtedly an intermediate in this reaction, but rearranges too rapidly to be isolated. In fact we have obtained spectroscopic evidence for the presence of small amounts of this nitrone in reaction mixtures containing benzaldehyde and N-triphenylmethylhydroxylamine which were heated to 65°.[11] By contrast, α,α-diphenyl-N-benzylnitrone can be easily prepared in good yield by this method at temperatures below 100° without loss through rearrangement.[1] Thus, in terms of nonbonded interactions of groups attached to carbon and nitrogen in the nitrone skeleton, it appears that a practical limit in the syn-

[7] O. Exner, *Chem. Listy*, **50**, 779 (1956); *Chem. Abstr.*, **50**, 15477*h* (1956).

[8] A. Hantzsch and F. Kraft, *Ber.*, **24**, 3511 (1891).

[9] P. L. Pickard and D. J. Vaughan, *J. Am. Chem. Soc.*, **72**, 876, 5017 (1950).

[10] T. Kubota, M. Yamakawa, and Y. Mori, *Bull. Chem. Soc. Japan*, **36**, 1552 (1963).

[11] E. J. Grubbs, unpublished results.

thetic method is reached in the preparation of the title compounds.

Experimental Section[12]

***p*-Methylbenzhydryl bromide** was prepared by the method of Singh, Andrews, and Keefer[13] and isolated in 88% yield as a pale yellow liquid, bp 135–137° (0.1 mm).

N-*p*-Methylbenzhydryl-α,α-diphenylnitrone (Ib).—A solution of potassium *t*-butoxide was prepared by dissolving 3.01 g (0.0770 g-atom) of freshly cut potassium in 100 ml of *t*-butyl alcohol. The excess *t*-butyl alcohol was distilled under an atmosphere of nitrogen. Benzene (100 ml) was then added and the distillation was continued for a few minutes to ensure removal of the alcohol. Benzophenone oxime (15.2 g, 0.0770 mole) in 150 ml of benzene was added to the potassium *t*-butoxide suspension. The reaction mixture was heated for 2 hr to ensure completion of the reaction. A solution of 20.0 g (0.0770 mole) of *p*-methylbenzhydryl bromide in 100 ml of benzene was then added to the yellow suspension of the oxime salt. The mixture was heated to boiling, with stirring, under an atmosphere of nitrogen for 45 hr. The cooled reaction mixture was filtered and the precipitated salt was rinsed with ether. The combined filtrate was concentrated to a viscous oil. The oil was dissolved in heptane at room temperature and allowed to concentrate by evaporation whereupon the crude nitrone (2.0 g, 7%) was deposited as pale yellow crystals, mp 116–122°. Recrystallization from hexane afforded the pure nitrone, mp 122.5–123.5°.

Anal. Calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71. Found: C, 86.00, 85.82; H, 6.34, 6.42; N, 3.83, 3.71.

The ultraviolet spectrum (in methylcyclohexane) shows a maximum at 310 mμ (*E* 16,200). The infrared spectrum obtained as a potassium bromide disk showed a weak band at 1375 cm^{-1} ($-CH_3$) and an intense band at 1210 cm^{-1} usually attributed to the nitrone N–O stretching vibration. The nmr spectrum (determined as a dilute solution in carbon tetrachloride) shows singlets at 2.34 ($-CH_3$) and 6.24 ppm (benzhydryl C–*H*) relative to tetramethylsilane, in addition to complex aromatic proton absorption in the region from 6.9 to 8.0 ppm. The ratios of integrated areas is in accord with the proposed structure.

Hydrolysis of α,α-Diphenyl-N-*p*-methylbenzhydrylnitrone.—A sample (0.0520 g, 0.138 mmole) of Ib was boiled in 4 ml of concentrated hydrochloric acid for 30 min. The reaction mixture was cooled and extracted with benzene. The benzene was removed using a stream of dry nitrogen. The residue was dried under vacuum, leaving 50.8 mg of a light yellow oil. The ultraviolet spectrum of this oil in ethanol showed a maximum at 252 mμ characteristic of benzophenone. The absorbance at 252 mμ was in close agreement with that calculated assuming the mixture to be comprised of only benzophenone and di-*p*-methylbenzhydryl ether. The oil was dissolved in 3 ml of dry hexane and the solution was saturated with dry hydrogen chloride. No precipitate formed, which suggests that N-*p*-methylbenzhydrylhydroxylamine is not present. Solvent was again removed from the sample. To the residual oil (47.1 mg) was added 0.0267 g (0.000135 mole) of 2,4-dinitrophenylhydrazine dissolved in 5 ml of absolute ethanol. A drop of concentrated hydrochloric acid was added and the solution was boiled for 10 min. The cooled solution deposited 35.0 mg (78%) of benzophenone 2,4-dinitrophenylhydrazone as bright orange crystals, mp 237–238.5° (lit.[14] mp 239°). The mixture melting point with an authentic sample was 238.5–240°. The filtrate remaining after isolation of this derivative was concentrated to an oil and then treated with α-naphthyl isocyanate. No urethan appeared to form.

Benzophenone O-*p*-Methylbenzhydryloxime (IIb).—A 0.110-g (0.292-mmole) sample of Ib was sealed in an evacuated Pyrex tube and heated at 200° for 35 min. The resulting light brown oil was dissolved in 2 ml of petroleum ether (bp 90–100°) containing a few drops of ether. After several days in a freezer, the solution deposited 90.4 mg (82%) of the oxime O-ether IIb, mp 61–62.5°. Recrystallization from a petroleum ether-ether mixture did not change the melting point. The ultraviolet spectrum in ethanol showed a single maximum at 264 mμ (*E* 13,800). The infrared spectrum (CCl_4) showed a weak band at 1375 cm^{-1} ($-CH_3$) and a weak band at 850 cm^{-1} attributable to the C–H out-of-plane vibration of a 1,4-disubstituted phenyl ring.

Anal. Calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71. Found: C, 85.70; H, 5.87; N, 3.49.

Alkylation of 4,4′-Dimethylbenzophenone Oxime with Benzhydryl Bromide.—A solution of potassium *t*-butoxide was prepared by dissolving 2.38 g (0.0608 g-atom) of potassium in 400 ml of dry *t*-butyl alcohol. To this solution was added 13.7 g (0.0608 mole) of 4,4′-dimethylbenzophenone oxime.[15] The mixture was heated and stirred to ensure complete formation of the oxime salt. Benzhydryl bromide (15.0 g, 0.0608 mole) was then added and the mixture was boiled under reflux, with stirring, for 1 hr. The reaction was run under an atmosphere of nitrogen. During this reaction time the pH of the mixture steadily dropped from an initial value of 11 to a final value of 6–7. The potassium bromide was separated by filtration and the filtrate was concentrated to a viscous oil. The oil was dissolved in petroleum ether from which a mixture of crystalline products was obtained in several crops, mp 76–112°. Repeated recrystallization of the crude mixture from methanol afforded 3.79 g (16%) of the oxime O-ether IIc, mp 107–108°. Concentration of the mother liquors and repeated recrystallization from heptane afforded 1.39 g of unreacted oxime, mp 165–167°. The recovery of this oxime from a reaction which, when stopped, exhibited a pH of 6–7 suggests that some of the benzhydryl bromide underwent solvolysis. The oxime O-ether isolated from this reaction was identical with IIc obtained from thermal isomerization of the corresponding nitrone and the complete characterization of IIc is described below. The ultraviolet spectra of several different mother liquors in the above recrystallizations showed a peak in the 310-mμ region, but the pure nitrone Ic could not be isolated.

N-Benzhydrylhydroxylamine was prepared by the method of Exner[7] in 75% yield, mp 71.5–74°. Recrystallization from cyclohexane provided the pure product in 46% yield, mp 75–76° (lit.[7] mp 75°).

Benzhydrylidenimine was prepared by the method of Hantzsch and Kraft[8] in 47% yield, mp 290°. Because of its tendency to sublime, literature values for the melting point vary. Thus Kaplan, Parton, and Vaughan[17] recorded a melting point of 310°. The melting range given by Lachman[18] is 230–250°.

Di-*p*-chlorophenyl Ketimine.—This ketimine was obtained by a method[9] previously described for the preparation of other diaryl ketimines. The molar ratio of *p*-chlorophenylmagnesium bromide to *p*-chlorobenzonitrile used was 1.5/1. After the free imine was liberated using anhydrous ammonia it was distilled to give a colorless oil which solidified in the receiver. The yield of colorless product was 58%, bp 138–144° (0.5 mm). Recrystallization of the ketimine from petroleum ether lowered the yield to 51%, mp 58–60°. A small sample was recrystallized two additional times from petroleum ether affording an analytically pure product, mp 59.5–60.5°.

Anal. Calcd for $C_{13}H_9Cl_2N$: C, 62.42; H, 3.63; Cl, 28.3; N, 5.60. Found: C, 62.79; H, 3.86; Cl, 28.4; N, 5.54.

Di-*p*-tolyl Ketimine was prepared by the method[9] previously described. The molar ratio of *p*-tolylmagnesium bromide to *p*-tolunitrile was 1.5/1. The ketimine was isolated by vacuum distillation, followed by two recrystallizations from petroleum ether, affording the pure product in 37% yield, mp 67–69° (lit.[9] mp 81°).

Because of the large discrepancy in melting points, the hydrochloride was prepared for comparison. A sample of the ketimine (0.213 g, 0.00102 mole) was dissolved in ether and the solution was saturated with anhydrous hydrogen chloride. A

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[12] All melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord recording spectrophotometer. The nmr spectra were obtained on a Varian Model A-70 spectrometer. The ultraviolet spectra were determined either on a Beckman Model DU or a Cary Model 14 recording spectrophotometer. The analyses were performed by West Coast Analytical Laboratories, Inc., and by C. F. Geiger Analytical Laboratory.

[13] A. Singh, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962).

[14] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "A Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 364.

[15] Prepared by the method reported for benzophenone oxime (A. Lachman, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1953, p 70) in quantitative yield, mp 166–167° (lit.[16] mp 162°).

[16] J. P. Picard and C. W. Kearns, *Can. J. Res.*, **B28**, 56 (1950).

[17] I. R. Kaplan, H. N. Parton, and J. Vaughan, *J. Am. Chem. Soc.*, **75**, 4341 (1953).

[18] See ref 15, p 234.

white granular solid (0.203 g, 81%) was obtained, mp 211–215° (lit.[9] mp 215°).

Condensations of Diaryl Ketimines with N-Benzhydrylhydroxylamine. General Procedure.—The condensations were carried out using an equimolar ratio of the two reactants (in the present work approximately 0.01-mole quantities were employed). The reactants were dissolved in approximately 30–40 ml of boiling petroleum ether (bp 90–100°). The solution was boiled under reflux in an atmosphere of nitrogen for periods ranging from 12 to 25 hr. Aliquots were removed from the reaction flask periodically and the extent of reaction was followed by the increase of ultraviolet absorption in the region of 310 mμ. When the ketimine hydrochloride is used, the free imine can be liberated into the petroleum ether by passing ammonia over the stirred suspension. The ammonium chloride may be separated from the solution after the condensation reaction is complete. The solution containing the reaction products was cooled and the crude nitrone separated from the solution in crystalline form.

α,α-Diphenyl-N-benzhydrylnitrone (Ia).—The free benzhydrylidenimine was liberated from the hydrochloride with ammonia. The reaction with N-benzhydrylhydroxylamine was carried out over a 25-hr period. Several recrystallizations of the crude product from ethanol afforded the pure nitrone in 45% yield, mp 163–165.5° (lit.[1] mp 162–166°, 165–167°). The nmr spectrum of Ia (obtained as a dilute solution in carbon tetrachloride) shows a singlet at 6.30 ppm (benzhydryl C-*H*) and complex aromatic proton absorption in the region from 7.2 to 8.1 ppm.

α,α-Di-*p*-tolyl-N-benzhydrylnitrone (Ic).—The condensation between di-*p*-tolylketimine and N-benzhydrylhydroxylamine was stopped after 12 hr. The product crystallized directly from the reaction solution in fair purity in a 62% yield, mp 136–140°. The nitrone was recrystallized three times from heptane to give analytically pure product, mp 136.5–138.5°.

Anal. Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44; N, 3.58. Found: C, 85.60; H, 6.42; N, 3.68.

The ultraviolet spectrum in ethanol exhibits a band at 310 mμ (*E* 15,500). The infrared spectrum (potassium bromide disk) showed a strong band at 1210 cm^{-1} attributed to the N→O stretch. The nmr spectrum (obtained as a dilute solution in carbon tetrachloride) showed a complex aromatic proton absorption in the region from 6.9 to 8.0 ppm, a singlet at 6.30 ppm (benzhydryl C*H*), and two singlets at 2.32 and 2.43 ppm (methyl protons). The ratios of integrated areas are consistent with the proposed structure.

***p,p*'-Dimethylbenzophenone O-Benzhydryloxime** (IIc).—The nitrone Ic (0.150 g, 0.383 mmole) was sealed in an evacuated Pyrex tube and heated at 200° for 35 min. The oil which remained after cooling the sample was triturated with a few drops of ether. The white solid which formed was recrystallized from aqueous ethanol, affording 0.081 g (54%) of the product, mp 106–107.5°. Two additional recrystallizations raised the melting point to 108–108.5°.

Anal. Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44; N, 3.58. Found: C, 85.55; H, 6.56; N, 3.72.

The ultraviolet spectrum (in ethanol) showed two maxima at 240 and 267 mμ (*E* 17,400 and 15,500). The nmr spectrum (in carbon tetrachloride) showed a complex aromatic multiplet centered at 7.19 ppm and singlets at 6.27 ppm (benzhydryl C–*H*) and at 2.37 and 2.27 ppm (methyl protons). The ratios of integrated areas are consistent with the proposed structure.

α,α-Di-*p*-chlorophenyl-N-benzhydrylnitrone (Id).—The reaction between di-*p*-chlorophenylketimine and N-benzhydrylhydroxylamine was stopped after 25 hr. The nitrone crystallized as pale yellow needles as the reaction solution was cooled. The yield was 39%, mp 147.5–150.5°. After two recrystallizations from heptane, the melting point range had changed very little, narrowing to 147.5–148.5°.

Anal. Calcd for $C_{26}H_{19}Cl_2NO$: C, 72.23; H, 4.43; Cl, 16.4; N, 3.24. Found: C, 72.00; H, 4.34; Cl, 16.7; N, 3.04.

The ultraviolet spectrum (in ethanol) showed a maximum at 312 mμ (*E* 15,900). The infrared spectrum (obtained as a potassium bromide disk) showed an intense band at 1220 cm^{-1} (N→O). The nmr spectrum (obtained as a dilute solution in carbon tetrachloride) revealed a complex aromatic proton absorption in the region from 7.1 to 8.1 ppm and a singlet at 6.22 ppm (benzhydryl C–*H*).

***p,p*'-Dichlorobenzophenone O-Benzhydryloxime** (IId).—A 0.194-g (0.383-mmole) sample of Id was sealed in an evacuated Pyrex tube and heated at 195° for 40 min. The product in the form of an oil was dissolved in aqueous ethanol and chilled to −20° for several days. The pale yellow crystals that slowly formed were collected and dried. The yield of IId melting at 73–76° was 0.115 g (59%). Three additional recrystallizations from aqueous ethanol lowered the yield to 31% and raised the melting point to 78.5–79°.

Anal. Calcd for $C_{26}H_{19}Cl_2NO$: C, 72.23; H, 4.43; Cl, 16.4; N, 3.24. Found: C, 72.26; H, 4.42; Cl, 16.7; N, 3.47.

The ultraviolet spectrum of IId (in ethanol) shows two maxima at 243 and 268 mμ (*E* 22,400 and 17,800).

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