Condensation of Aromatic Nitro Compounds with Arylacetonitriles.[1,2] IV. Some Reactions of the Arylcyanomethylenequinone Oximes

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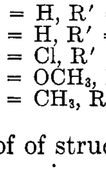
The hydrogen peroxide oxidation of arylcyanomethylenequinone oximes yields 4-nitrobenzophenones. The conversion of arylcyanomethylenequinone oximes to 4,4′-diaroylazoxybenzenes is also reported.

Since the arylcyanomethylenequinone oximes[2,4] produced by the condensation of aromatic nitro compounds with arylacetonitriles are new compounds, we decided to initiate a systematic investigation of the chemical reactions which they undergo. In order to keep the investigation within reasonable bounds and at the same time in order to ensure ourselves that we were studying chemical reactions which were somewhat general in scope, we decided to limit our investigation, for the present at least, to the following six arylcyanomethylenequinone oximes, which we considered as representative of the compounds thus far prepared: 4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (I), α-(*p*-chlorophenyl)-4-oxo-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (II), α-(*p*-methoxyphenyl)-4-oxo-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (III), 3-chloro-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (IV), 3-methoxy-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (V), and 3-methyl-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (VI).



I. R, R′ = H
II. R = H, R′ = Cl
III. R = H, R′ = OCH_3
IV. R = Cl, R′ = H
V. R = OCH_3, R′ = H
VI. R = CH_3, R′ = H

As part of the proof of structures for the arylcyanomethylenequinone oximes, we previously reported the hydrogen peroxide oxidation of I, II, and III to *p*-nitrobenzophenones.[4] Since we had need for the *p*-nitrobenzophenones, as will subsequently be shown, we repeated these reactions. In addition, VI was oxidized with hydrogen peroxide, yielding 3-methyl-4-nitrobenzophenone, a known compound.[5] Comparison of our product with an authentic sample of 3-methyl-4-nitrobenzophenone[6] in regard to melting points, mixture melting point, and infrared spectra, showed the samples were identical. The hydrogen peroxide oxidation of IV produced 3-chloro-4-nitrobenzophenone, a new compound. The structure of the product was ascertained through reduction to the known 4-amino-5-chlorobenzophenone,[7] whose known acetyl derivative was likewise prepared. The oxidation of V with hydrogen peroxide yielded 3-methoxy-4-nitrobenzophenone, a new compound. A 2,4-dinitrophenylhydrazone derivative was prepared from this ketone. Its infrared spectrum compared favorably with the infrared spectra of the other nitrobenzophenones, showing an absorption peak at 6.0 μ, characteristic of a benzophenone carbonyl group,[8] and absorption peaks at 6.52 μ and 7.35 μ, characteristic of the nitrogen-oxygen stretching vibrations of aromatic nitro compounds.[9] No further attempt was made to prove the structure of the product. We considered that by proving the structures of five of the oxidation products, we had established the course of this oxidation reaction. There was, therefore, no reason to suspect that this one remaining case should have a different outcome.

Since a variety of arylcyanomethylenequinone oximes can be prepared, and since the oxidation products can be obtained in good yield, 61 to 91% in the present investigation, we suggest the hydrogen peroxide oxidation of the arylcyanomethylenequinone oximes as a convenient route to many 4-nitrobenzophenones which otherwise might be difficult to prepare. In order to represent the oxidation reaction which apparently involves a 1,6-attack on the quinoid system, we offer the following general equation in which Q signifies a *p*-quinoid structure and Ar′ signifies a *p*-bivalent aromatic radical hav-

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[1] Research project supported in part by National Science Foundation Grants, NSF-G10030 and NSF-G19165.

[2] Previous paper, *J. Org. Chem.*, **26**, 4270 (1961).

[3] Part of a dissertation submitted by Joseph D. Benigni to the University of Notre Dame in partial fulfillment of the requirements for the Ph.D. degree, February 1962.

[4] R. B. Davis, L. C. Pizzini, and J. D. Benigni, *J. Am. Chem. Soc.*, **82**, 2913 (1960).

[5] L. Chardonnens and W. Schlapbach, *Helv. Chim. Acta*, **29**, 1413 (1946).

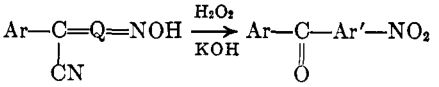
[6] The sample was generously supplied by Dr. L. Chardonnens, University of Fribourg, Switzerland.

[7] F. D. Chattaway, *J. Chem. Soc.*, **85**, 340 (1904).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 137.

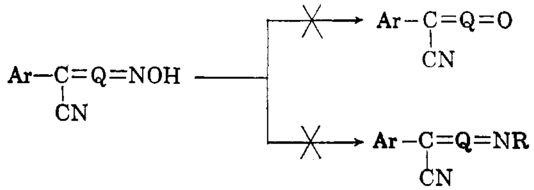
[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 298.

ing the same chemical formula and arrangement of substituents as Q.



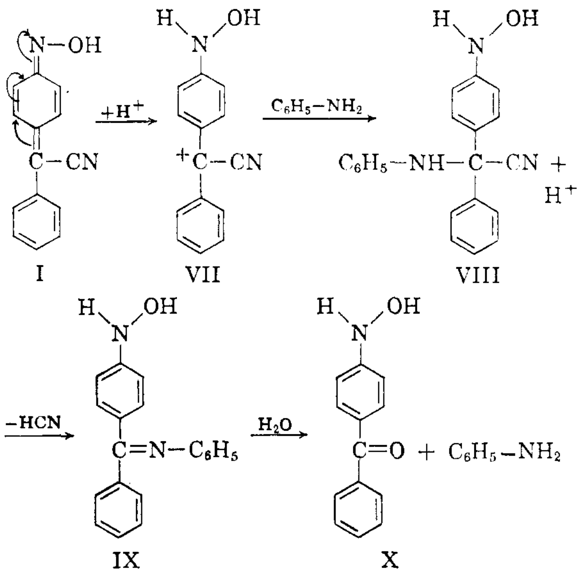
$$\mathrm{Ar{-}\underset{\underset{CN}{|}}{C}{=}Q{=}NOH \xrightarrow[KOH]{H_2O_2} Ar{-}\underset{\underset{O}{\|}}{C}{-}Ar'{-}NO_2}$$

Many attempts were made to hydrolyze or otherwise convert the hydroxyimino group of the arylcyanomethylenequinone oximes to the oxo, imino, or substituted imino group as represented in the following scheme in which R signifies hydrogen, an alkyl, or an aryl group. None of the experiments produced the desired result. We were led to conclude that the carbon to nitrogen double bond in these quinone oximes is not readily susceptible to attack. From evidence gleaned in this and subsequent investigations, the reason for our failures seems to be that the quinone oximes are much more susceptible to 1,6-attack, that is, attack involving the nitrogen atom of the hydroxyimino group and the carbon atom holding the cyano group.



In what may be considered as attempts to convert the hydroxyimino group to the phenylimino group in 4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (I), samples of I were allowed to stand in a solution of aniline in glacial acetic acid and also in a solution of aniline in methanol containing a small amount of concentrated hydrochloric acid. Both reaction mixtures produced the same compound which evidently was not the desired phenylimino derivative. The melting points, infrared spectra, and elemental analyses suggested that the product was 4,4′-dibenzoylazoxybenzene, a known compound.[10] As confirmatory evidence for the structure of our product, we independently synthesized 4,4′-dibenzoylazoxybenzene by the reaction of *p*-nitrobenzophenone in methanolic potassium hydroxide solution containing a small amount of paraformaldehyde. The latter was added because other workers had reported improved yields of azoxy compounds when small amounts of an aldehyde were used in similar reactions.[11] The melting points, mixture melting point, and infrared spectra of samples prepared by the alternate paths indicated the products were identical.

In order to explain the formation of 4,4′-dibenzoylazoxybenzene from the quinone oxime (I), the following reaction scheme is offered, showing the production of *p*-hydroxylaminobenzophenone (X) which subsequently is transformed to the azoxy product.



We propose that the mechanism of the reaction initially involves the acid-catalyzed 1,6-addition of aniline to I, followed by the elimination of hydrogen cyanide and subsequent hydrolysis to form X. It has been pointed out to us that the mechanism could be greatly simplified by postulating the acid-catalyzed 1,6-addition of water to I followed by the elimination of hydrogen cyanide to form X. While this proposal would indeed simplify the picture, nevertheless we believe that it would not represent what actually happens at least not in the reactions conducted in glacial acetic acid. We used reagent grade aniline and reagent grade glacial acetic acid. It seems unlikely to us that the intermediate cation VII should wait for traces of water molecules when many more molecules and more basic molecules of aniline are readily available. At the same time we do not wish to exclude this possibility entirely since our own mechanism postulates that intermediate IX does find the traces of water molecules.

Arylhydroxylamino compounds, when allowed to stand in solution, are known to form azoxy compounds.[12] This transformation is thought to take place by way of intermolecular oxidation-reduction of the hydroxylamino compound to produce an amine and a nitroso compound, the latter condensing with unchanged hydroxylamino compound to yield the azoxy product.[12] Hence the transformation of the proposed intermediate X to 4,4′-dibenzoylazoxybenzene is not unexpected. At the same time, we would like to point out that we have obtained evidence which suggests that the oxidation of the hydroxylamino compound X does not take place entirely by way of intermolecular oxidation-reduction. We conducted two distinct experiments involving I dissolved in a solution of methanol and

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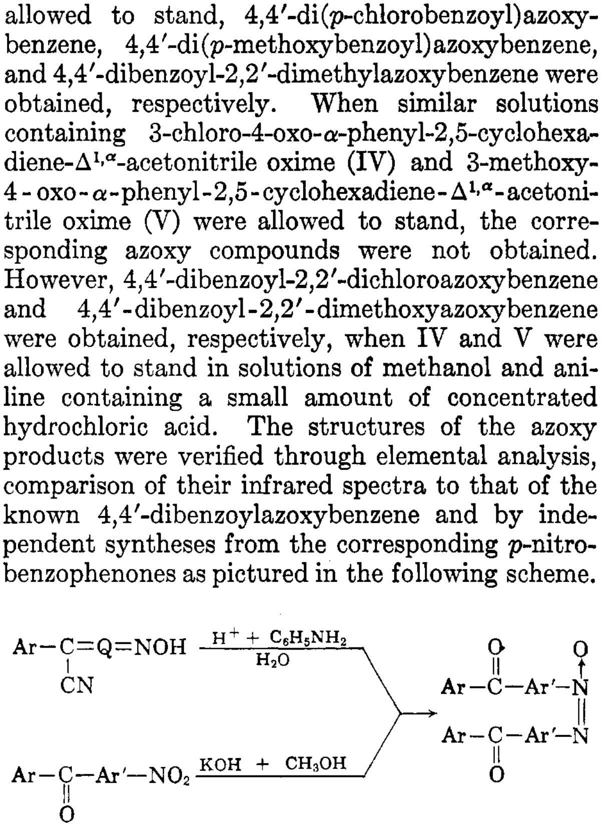
(10) Y. Ishander and R. Tewfik, *J. Chem. Soc.*, 2058 (1951).

(11) D. H. Richardson, *J. Chem. Soc.* **129**, 522 (1926).

(12) N. V. Sidgwick, "The Organic Chemistry of Nitrogen Compounds," Oxford University Press, London, 1937, p. 163.

aniline containing a small amount of concentrated hydrochloric acid. Both experiments were conducted under identical conditions with the exception that one reaction mixture was left exposed to the air, while the second reaction was conducted under an atmosphere of nitrogen. Both reaction mixtures produced 4,4′-dibenzoylazoxybenene, the former in 49% yield, the latter in 16% yield, suggesting that the oxidation of *p*-hydroxylaminobenzophenone (X) to the corresponding nitroso compound is assisted by oxygen present in the air.

When solutions containing α-(*p*-chlorophenyl)-4-oxo-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (II), α-(*p*-methoxyphenyl)-4-oxo-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (III), and 3-methyl-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (VI) in glacial acetic acid and aniline were allowed to stand, 4,4′-di(*p*-chlorobenzoyl)azoxybenzene, 4,4′-di(*p*-methoxybenzoyl)azoxybenzene, and 4,4′-dibenzoyl-2,2′-dimethylazoxybenzene were obtained, respectively. When similar solutions containing 3-chloro-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (IV) and 3-methoxy-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (V) were allowed to stand, the corresponding azoxy compounds were not obtained. However, 4,4′-dibenzoyl-2,2′-dichloroazoxybenzene and 4,4′-dibenzoyl-2,2′-dimethoxyazoxybenzene were obtained, respectively, when IV and V were allowed to stand in solutions of methanol and aniline containing a small amount of concentrated hydrochloric acid. The structures of the azoxy products were verified through elemental analysis, comparison of their infrared spectra to that of the known 4,4′-dibenzoylazoxybenzene and by independent syntheses from the corresponding *p*-nitrobenzophenones as pictured in the following scheme.



The expected azoxy compounds were isolated from the reactions of 4-chloro-4′-nitrobenzophenone, 4-methoxy-4′-nitrobenzophenone, and 2-methoxy-4-nitrobenzophenone in methanolic potassium hydroxide solutions containing a small amount of paraformaldehyde. Under similar reaction conditions, we were unsuccessful in attempts to obtain azoxy compounds from 3-methyl-4-nitrobenzophenone and 3-chloro-4-nitrobenzophenone. The reaction of the latter produced a compound which apparently was 4,4′-dibenzoyl-2,2′-dichloroazobenzene. When paraformaldehyde was not used in the reaction mixture, 3-chloro-4-nitrobenzophenone produced the expected azoxy compound in low yield. When stannous chloride[13] was used in place of paraformaldehyde, we did obtain the azoxy compound from 3-methyl-4-nitrobenzophenone. In view of the work of other investigators,[14] it is not at all surprising that the same set of reaction conditions did not produce azoxy compounds in all cases.

Samples of the corresponding azoxy compounds obtained from the quinone oximes and from the *p*-nitrobenzophenones were compared with regard to melting points, mixture melting points, and infrared spectra, and were found to be identical.

Experimental[15,16]

Arylcyanomethylenequinone oximes (I–VI) were prepared according to methods previously described.[2,4]

***p*-Nitrobenzophenone, 4-chloro-4′-nitrobenzophenone and 4-methoxy-4′-nitrobenzophenone** were likewise prepared according to methods previously described.[4]

3-Methyl-4-nitrobenzophenone.—In a manner similar to that previously described,[4] to a solution of 10 g. (0.042 mole) of 3-methyl-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (VI) in 300 ml. of water, 100 ml. of methanol, and 30 g. (0.45 mole) of potassium hydroxide (assay 85%) was added 60 g. (0.53 mole) of 30% hydrogen peroxide. There was obtained 9.3 g. of 3-methyl-4-nitrobenzophenone (91% yield), m.p. 126–130°, recrystallized from 95% ethanol, m.p. 134–135° (lit.,[5] m.p. 134–135°), mixture melting point with an authentic sample[6] 134–135°. The infrared spectra of the product and the authentic sample were superimposable, showing significant absorption bands at 6.05, 6.55, and 7.38 μ.

3-Chloro-4-nitrobenzophenone.—Following an identical procedure, 10 g. (0.039 mole) of 3-chloro-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (IV) produced 9.1 g. (89% yield) of 3-chloro-4-nitrobenzophenone, m.p. 89–92°, recrystallized from methanol–water, m.p. 94–96°. The infrared spectrum of the product possessed significant absorption bands at 6.05, 6.55, and 7.32 μ.

Anal. Calcd. for $C_{13}H_8ClNO_3$: C, 59.67; H, 3.08; Cl, 13.55. Found: C, 60.07; H, 3.26; Cl, 13.55.

The 2,4-dinitrophenylhydrazone derivative, prepared from 0.5 g. of the above ketone in 72% yield according to the procedure of Shriner, Fuson, and Curtin,[17] melted at 225–229°, recrystallized from benzene, m.p. 237–238°.

Anal. Calcd. for: $C_{19}H_{11}ClN_5O_6$: C, 51.77; H, 2.51; Cl, 8.04. Found: C, 51.89; H, 2.75; Cl, 8.05.

To a solution of 2 g. (0.0076 mole) of 3-chloro-4-nitrobenzophenone, 50 ml. of methanol, and 25 ml. (0.44 mole) of glacial acetic acid was added 2 g. (0.03 mole) of zinc dust. This mixture was heated at 50–60° for 15 min., allowed to cool, and filtered. The filtrate was poured into 200 ml. of water whereupon 4-amino-3-chlorobenzophenone precipitated as a colorless solid. The product was isolated in 85% yield (1.5 g.) by filtration, m.p. 128–132°, recrystallized from chloroform–petroleum ether (b.p. 60–71°), m.p. 137–139° (lit.,[7] 140°).

3-Methoxy-4-nitrobenzophenone.—In an identical manner, there was obtained from 10 g. (0.039 mole) of 3-methoxy-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile oxime (V) 8.5 g. (83% yield) of 3-methoxy-4-nitrobenzophenone, m.p. 85–87°, recrystallized from methanol–water, m.p. 92–94°. The infrared spectrum of the product possessed significant absorption bands at 6.0, 6.52, and 7.35 μ.

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(13) R. Meldola and E. R. Andrews, *J. Chem. Soc.*, **69**, 7 (1896).

(14) H. E. Bigelow, *Chem. Revs.*, **9**, 155 (1931).

(15) Analyses by Midwest Microlab, Inc., Indianapolis, Ind.

(16) All melting points are uncorrected.

(17) R. L. Shriner, R. C. Fuson, and D. G. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, 1956, p. 219.

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31. Found: C, 65.53; H, 4.34.

In the manner previously referred to,[17] the 2,4-dinitrophenylhydrazone derivative, prepared from 0.5 g. of the above ketone in 60% yield, melted at 249–255° dec., recrystallized from methanol, m.p. 265–266° dec.

Anal. Calcd. for $C_{20}H_{15}N_5O_7$: 54.92; H, 3.46; N, 16.01. Found: C, 55.02; H, 3.57; N, 15.82.

4,4′-Dibenzoylazoxybenzene. A. From 4-Oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile Oxime (I). Procedure 1.—To a solution of 5 g. (0.022 mole) of I in 100 ml. of glacial acetic acid was added 15 g. of aniline. The reaction mixture was allowed to stand exposed to air at room temperature for 2 weeks, during which time a yellow solid precipitated. The solid was then isolated by filtration, washed with hot methanol, and dried. There was obtained 1.7 g. (37% yield) of 4,4′-dibenzoylazoxybenzene, m.p. 199–200°, recrystallized from benzene as yellow plates, m.p. 203–204° (lit.,[10] 200°).

Anal. Calcd. for $C_{26}H_{18}N_2O_3$: C, 76.83; H, 4.46; N, 6.89. Found: C, 76.98; H, 4.47; N, 6.94.

Procedure 2.—To a solution of 5 g. (0.022 mole) of I in 100 ml. of methanol and 15 g. of aniline was added 5 ml. of concd. hydrochloric acid. The reaction mixture was allowed to stand exposed to air at room temperature for 2 weeks. The product was isolated as in A1 above in 49% yield (2.29 g.), m.p. 197–199°, recrystallized from benzene, m.p. 202–203°, mixture melting point with a sample from A1, 202–204°. Infrared spectra of the two samples were superimposable.

Procedure 3.—Following a procedure identical to A2, with the exceptions that nitrogen was bubbled through the methanol–aniline solution before the introduction of I and the reaction mixture was allowed to stand under an atmosphere of nitrogen, there was obtained 0.7 g. of product (16% yield), m.p. 201–202°, recrystallized from benzene, m.p. 203–204°.

B. From *p*-Nitrobenzophenone.—To a solution of 10 g. of potassium hydroxide (assay 85%) in 100 ml. of methanol was added 2 g. (0.0088 mole) of *p*-nitrobenzophenone and 0.1 g. of paraformaldehyde. The mixture was heated at reflux for 0.5 hr. and then allowed to cool. The yellow solid which precipitated was isolated as in A1 above. There was obtained 1.05 g. (59% yield) of 4,4′-dibenzoylazoxybenzene, m.p. 200–201°, recrystallized from benzene, 202–204°, mixture melting point with a sample produced as in A1, 202–204°. Infrared spectra of the two samples were superimposable.

4,4′-Di(*p*-chlorobenzoyl)azoxybenzene. A. From α-(*p*-Chlorophenyl)-4-oxo-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile Oxime (II).—Following the procedure described in A1 above, there was obtained from 5 g. (0.019 mole) of II 1.5 (32% yield) of 4,4′-di(*p*-chlorobenzoyl)azoxybenzene, m.p. 260–266°, recrystallized from chloroform–methanol, m.p. 290–292°.

Anal. Calcd. for $C_{26}H_{16}Cl_2N_2O_3$: C, 65.68; H, 3.39; Cl, 14.92. Found: C, 65.81; H, 3.47; Cl, 15.02.

B. From 4-Chloro-4′-nitrobenzophenone.—Following the procedure described in B above, 2 g. (0.0076 mole) of 4′-chloro-4′-nitrobenzophenone produced 0.6 g. (33% yield) of 4,4′-di(*p*-chlorobenzoyl)azoxybenzene, m.p. 284–288°, recrystallized from chloroform–methanol, m.p. 291–293°, which was not depressed when mixed with a sample obtained from procedure A. The infrared spectra of the two samples were superimposable.

4,4′-Di(*p*-methoxybenzoyl)azoxybenzene. A. From α-(*p*-Methoxyphenyl)-4-oxo-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile Oxime (III).—In the manner of A1 above, 5 g. (0.02 mole) of III produced 2.5 g. (54% yield) of 4,4′-di(*p*-methoxybenzoyl)azoxybenzene, m.p. 244–246°, recrystallized from benzene, m.p. 247°.

Anal. Calcd. for $C_{28}H_{22}N_2O_5$: C, 72.09; H, 4.75; N, 6.01. Found: C, 72.15; H, 4.87; N, 5.81.

B. From 4-Methoxy-4′-nitrobenzophenone.—Using procedure B above, 2 g. (0.0078 mole) of 4-methoxy-4′-nitrobenzophenone gave 0.9 g. (50% yield) of 4,4′-di(*p*-methoxybenzoyl)azoxybenzene, m.p. 242–245°, recrystallized from benzene, m.p. 246–247°, not depressed on mixing with a sample obtained by procedure A. The infrared spectra of the two samples were superimposable.

4,4′-Dibenzoyl-2,2′-dimethylazoxybenzene. A. From 3-Methyl-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile Oxime (VI).—According to the procedure of A1 described above, 5 g. (0.021 mole) of VI produced 2.5 g. (54% yield) of 4,4′-dibenzoyl-2,2′-dimethylazoxybenzene, m.p. 152–155°, recrystallized from benzene–methanol, m.p. 158–160°.

Anal. Calcd. for $C_{28}H_{22}N_2O_3$: C, 77.40; H, 5.10; N, 6.45. Found: C, 77.70; H, 4.94; N, 6.04.

B. From 3-Methyl-4-nitrobenzophenone.—One gram (0.0041 mole) of the ketone and 1.8 g. of stannous chloride dihydrate were added to a solution of 7 g. of potassium hydroxide (assay 85%) in 70 ml. of methanol. The mixture was heated at reflux for 1 hr. Upon cooling, 0.55 g. (61%) yield) of 4,4′-dibenzoyl-2,2′-dimethylazoxybenzene was isolated in the usual manner, m.p. 155–157°, recrystallized from benzene, m.p. 158–160°, not depressed on mixing with a sample obtained from procedure A. The infrared spectra of the two samples were superimposable.

4,4′-Dibenzoyl-2,2′-dichloroazoxybenzene. A. From 3-Chloro-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile Oxime (IV).—Following the method of procedure A2 above, 5 g. (0.019 mole) of IV gave 1.3 g. (27% yield) of 4,4′-dibenzoyl-2,2′-dichloroazoxybenzene, m.p. 173–178°, recrystallized from benzene, m.p. 185–186°.

Anal. Calcd. for $C_{26}H_{16}Cl_2N_2O_3$: C, 65.68; H, 3.39; Cl, 14.92. Found: C, 66.05; H, 3.57; Cl, 14.62.

B. From 3-Chloro-4-nitrobenzophenone.—One gram (0.0038 mole) of the ketone was heated at reflux in a solution of 2.5 g. of potassium hydroxide (assay 85%) in 50 ml. of methanol for 2 hr. Upon cooling and isolating the precipitated material in the usual manner, there was obtained 0.1 g. (10% yield) of 4,4′-dibenzoyl-2,2′-dichloroazoxybenzene, m.p. 175–179°, recrystallized from chloroform–methanol, m.p. 185–186°, not depressed on mixing with a sample obtained from procedure A above. The infrared spectra of the two samples were superimposable.

4,4′-Dibenzoyl-2,2′-dimethoxyazoxybenzene. A. From 3-Methoxy-4-oxo-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetonitrile Oxime (V).—According to the procedure of A2 above, 5 g. (0.02 mole) of V produced 1.5 g. (32% yield) of 4,4′-dibenzoyl-2,2′-dimethoxyazoxybenzene, m.p. 168–172°, recrystallized from benzene–methanol, m.p. 175–177°.

Anal. Calcd. for $C_{28}H_{22}N_2O_5$: C, 72.09; H, 4.75; N, 6.01. Found: C, 72.20; H, 5.06; N, 5.76.

B. From 3-Methoxy-4-nitrobenzophenone.—Following method B above for the preparation of 4,4′-dibenzoylazoxybenzene, 2 g. (0.0078 mole) of 3-methoxy-4-nitrobenzophenone gave 1 g. (55% yield) of 4,4′-dibenzoyl-2,2′-dimethoxyazoxybenzene, m.p. 175–176°, recrystallized from benzene, m.p. 177–178°, not depressed on mixing with a sample obtained from procedure A. The infrared spectra of the two samples were superimposable.

4,4′-Dibenzoyl-2,2′-dichloroazobenzene.—When 2 g. (0.0076 mole) of 3-chloro-4-nitrobenzophenone, 10 g. of potassium hydroxide (assay 85%), 0.1 g. of paraformaldehyde, and 50 ml. of methanol were heated at reflux for 90 min., cooled and the product isolated in the usual manner, there was obtained 0.52 g. (30% yield) of 4,4′-dibenzoyl-2,2′-dichloroazobenzene, m.p. 176–180°, recrystallized as red needles from benzene, m.p. 187–188°.

Anal. Calcd. for $C_{26}H_{16}Cl_2N_2O_3$: C, 67.97; H, 3.51; Cl, 15.43. Found: C, 67.71; H, 3.45; Cl, 15.15.