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The Reaction of N, N-Disubstituted Ketohydrazones with Lead Tetraacetate

Elisabeth Cerda

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THE REACTION OF N,N-DISUBSTITUTED KETOHYDRAZONES
WITH LEAD TETRAACETATE

A Thesis
Presented to
The Faculty of the School of Graduate Studies
Western Michigan University

In partial fulfillment
of the requirement for
the degree of Master of Arts
in Chemistry

by
Elisabeth Cerda (Mrs.)
Kalamazoo, Michigan
June 1961

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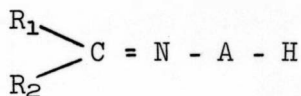
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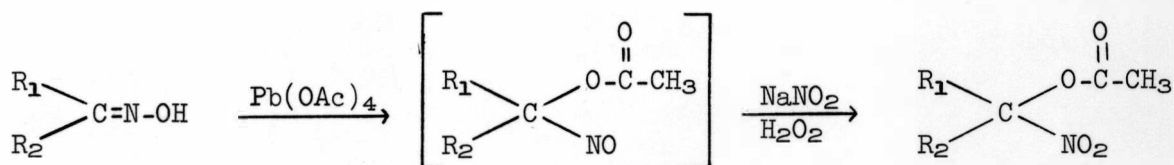
Acknowledgment is also hereby given to the National Science Foundation for financial assistance rendered for this project.

INTRODUCTION

The reaction of lead tetraacetate with compounds of the following general structure

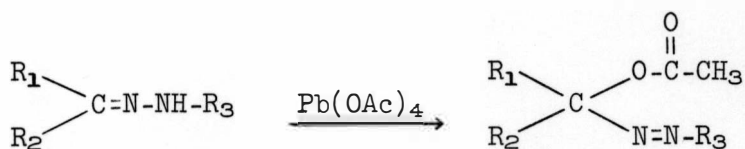


was first reported by Iffland and Criner (12). In the case of ketoximes (A = oxygen), a nitrosoacetate was produced which was oxidized to the more stable acetoxy-nitrocompound as follows:



The generality of the reaction was established by preparation of a series of acetoxy-nitrocompounds from alicyclic and aliphatic ketoximes. The apparently similar reaction of cyclohexanonephenylhydrazone (A = N-φ) with lead tetraacetate was reported, but the reaction product was not identified.

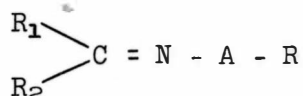
Further examination of this related reaction of hydrazones by Iffland, Salisbury and Schafer (13) led to the development of a general method for the preparation of a new class of compounds and identification of their structure.



In this way fourteen azoacetates were synthesized with various alicyclic, aliphatic and aromatic groups at R_1 , R_2 , and R_3 .

A free radical type mechanism was proposed for the reaction, and reaction rate studies indicated that the reaction followed second order kinetics.

Investigation of the reactions of lead tetraacetate was extended to compounds of the general type formula



It was reported (13) that cyclohexanone^{oxime}~~N~~-O-methyl ether, having $A = \text{oxygen}$, did not react with lead tetraacetate and could be recovered in 89% yield.

In view of these observations, it was expected that disubstituted hydrazones for which $A = N-R$ or $N-\phi$ would also be unreactive with lead tetraacetate. However, it has been found, that lead tetraacetate does react with disubstituted hydrazones, but the nature of this reaction and its products had not been further investigated at the time of the present study.

This seemingly anomalous reaction behavior of the disubstituted hydrazones was made the starting point for the work presented in the following sections. Ultimately, the determination of the reaction stoichiometry, the identification of reaction products and the demonstration of the general nature of this reaction was realized.

EXPERIMENTAL PART

In the following experimental section all melting points and boiling points are uncorrected. All temperatures are expressed as degrees centigrade.

The ultraviolet spectra were measured with a Beckman Model DU spectrophotometer with the compounds dissolved in 95% ethanol. This data has been graphed as k vs. wave length in $m\mu$, where k is the specific extinction coefficient of the substance and is defined as $k = A/bC$. A is the absorbance, b is the length of light path through the sample (1 cm.), and C is the concentration of the solution in g./liter (21). The quantity ϵ , which appears in Table I and was used for certain calculations of percent yield, represents the generally reported molar extinction coefficient and can be obtained by multiplying k by the molecular weight of the compound.

The infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer and the assignment of bands was made according to Bellamy (2).

Gas-liquid chromatography was carried out with an Aerograph Gas Chromatograph Model A-90-C using a diethyleneglycolsuccinate column.

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Lead tetraacetate was purchased from Arapahoe Chemicals (#908, technical). The reagent was moist with acetic acid and analysis by conversion to lead dioxide showed an average minimum lead tetraacetate content of 95.6%. Weights of lead tetraacetate used in the experiments were calculated assuming 95% purity of the reagent.

A. Preparation of Hydrazones

The properties of all hydrazones prepared and used are collected in Table I.

1.) Benzophenone-N,N-dimethylhydrazone and Acetone-N-methyl-N-phenylhydrazone were available at the beginning of this work.

2.) Benzophenone-N-methyl-N-phenylhydrazone

To a solution of 13.60 g. (0.075 moles) of benzophenone in 70 ml. of absolute alcohol, 9.20 g. (0.075 moles) of N-methyl-N-phenylhydrazine (student preparation) and 5 ml. of glacial acetic acid were added, and the mixture was refluxed for 22 hrs. On cooling the reaction mixture, yellow crystals precipitated which were recrystallized twice from 95% ethanol and melted at 73-78°. The reaction gave the hydrazone in 47% yield. [Literature value: m.p. 81-82°, yellow crystals (4)].

3.) Benzophenone-N-ethyl-N-phenylhydrazone

a.) N-nitroso-N-ethylaniline

The method of Hartman and Roll (9) was adapted for the preparation of N-nitroso-N-ethylaniline from ethylaniline, hydrochloric acid and sodium nitrite. The product (from 1.0 moles of ethylaniline) was distilled under reduced pressure and six fractions of yellow oil were collected. The nitroso-compound was obtained in 91% yield, based on fractions 2 - 5, b.p. 124-126.5° at 12 mm, $n_D^{22.5}$ 1.5586-1.5591. [Literature values: b.p. 119.5-120° at 15 mm. (7); 133° at 19 mm. (17); 96-97° at 1.9 mm. (18)].

b.) N-ethyl-N-phenylhydrazine

This compound was prepared by lithium aluminum hydride reduction of 0.1 moles of the N-nitroso-N-ethylaniline following a procedure by Hanna and Schueler (8). The formation of a pink complex, which takes place with the methylphenyl compound according to the reference, was not observed with the

ethylphenyl compound. Distillation of the reaction product under reduced pressure yielded the hydrazine with unreacted nitrosocompound present in the later fractions. All fractions were combined and dissolved in dilute hydrochloric acid. The nitrosamine was removed from this solution by extraction with petroleum ether (30-60°), and the free hydrazine was regenerated by adding the hydrochloric acid solution to a 20% sodium hydroxide solution. The hydrazine, a light yellow oil, was separated from the aqueous layer and the latter was extracted several times with petroleum ether (30-60°). The combined oil and ether extracts were dried with anhydrous potassium carbonate; the solvent was evaporated and the residue was distilled at reduced pressure. Six fractions of crude N-ethyl-N-phenylhydrazine, b.p. 78-101° at 6 mm., $n_D^{23.5}$ 1.5513 - 1.5652, were collected. The yield of crude product was 68% of theory.

c.) Benzophenone-N-ethyl-N-phenylhydrazone

For the synthesis of this hydrazone 16.38 g. (0.09 moles) of benzophenone was dissolved in a minimum amount (10 ml.) of absolute alcohol. To this solution, 8.50 g. (0.062 moles) of the crude N-ethyl-N-phenylhydrazine and 4 drops of glacial acetic acid were added and the mixture was refluxed for 4 1/2 days. The orange-yellow reaction mixture was cooled and the alcohol evaporated, leaving 24.50 g. of orange-yellow oil which did not crystallize. This oil was distilled at reduced pressure and fractions boiling up to 180° at 4 mm. were collected (a mixture of starting hydrazine and benzophenone). The residue, approximately 9.0 g., solidified on cooling and stirring. After two recrystallizations from 95% ethanol, 7.65 g. of bright orange crystals (41% of theory) were obtained. Analysis, calculated for $C_{21}H_{20}N_2$: N, 9.33; found: N, 9.27.

4.) Benzophenone-N,N-diphenylhydrazone

Adapting a procedure by Adams and Johnson (1), 13.25 g. (0.06 moles) of diphenylhydrazine hydrochloride (Eastman Organic Chemicals #954) and 20.40 g. (0.15 moles) of sodium acetate were dissolved in a mixture of 30 ml. of water and 150 ml. of ethanol. After addition of 10.92 g. (0.06 moles) of benzophenone the reaction mixture was refluxed for 65 hrs. Cooling the mixture produced crystals which were filtered and recrystallized from an ethanol-water mixture. The purified product of greenish-yellow needles weighed 6.60 g. (31.5% of theory), m.p. 145-147°. [Literature values: m.p. 145.5° (4), 145° (5)].

5.) Acetonephenylhydrazone

After adding 34.8 g. (0.6 moles) of acetone to 57.0 g. (0.5 moles) of phenylhydrazine (Eastman Organic Chemicals #329) with stirring, the resulting mixture was heated for one hour. The reaction mixture was then cooled and after addition of 200 ml. of petroleum ether (20-40°) the excess acetone was removed by washing with two 100-ml. portions of water. The petroleum ether solution was dried over anhydrous sodium sulfate; the solvent was evaporated and the residue distilled under reduced pressure, yielding 58.5 g. of yellow oil, b.p. 137-141° at 13 mm., n_D^{22} 1.5870 - 1.5876, (79% of theory). [Literature values: m.p. 26.6°, b.p. 163° at 50 mm. (14)].

TABLE I
PROPERTIES OF HYDRAZONES

Structure of Compound	Appearance	m.p. °C	b.p. °C	P mm.	n _D	Ultraviolet Absorption	
(a)						λ_{max} mμ	log ε _{max}
	yellow liquid, partially crystallizes at room temp.		179-180 146-148	15 1	1.6049 (b) 1.6046- 1.6048	241 320	4.13 3.60
(c)							
	bright yellow crystals	73-78				258 365	4.45 3.87
	bright orange crystals	72-73				254 368	4.32 3.71
(d)							
	green-yellow needles	145-147				248 300 360	4.38 3.98 3.89
	dark yellow oil		88-89	3	(e) 1.5540- 1.5546		
(f)							
	yellow oil		137-139	13	(g) 1.5862		
(h)							
	tan crystals	133-136				238 294 340	4.23 4.07 4.27

Footnotes for Table I

- (a) Prepared by L. Salisbury, Analysis, calculated for $C_{15}H_{16}N_2$: N, 12.51;
found: N, 12.47.
- (b) $t = 28^\circ$
- (c) Literature value: yellow crystals, m.p. $81-82^\circ$ (4).
- (d) Literature value: citron-yellow needles, m.p. 145.5° (4).
- (e) $t = 25^\circ$
- (f) Literature values: b.p. 163° at 50 mm., 160° at 44 mm., 153° at 31 mm.,
 140° at 16 mm.; m.p. 26.6° (3).
- (g) $t = 24^\circ$
- (h) Literature value: m.p. $137-138^\circ$ (11).

B. Reactions of N,N-disubstituted Ketohydrazones with Lead Tetraacetate1.) Determination of Stoichiometry of the Reaction

A solution of 1.12 g. (0.005 moles) of benzophenone-N,N-dimethylhydrazone in methylene chloride was prepared and diluted to exactly 25 ml. (concentration: 0.2 moles/liter).

Lead tetraacetate was freed from acetic acid by several successive washings with petroleum ether ($20-40^\circ$) and final removal of the ether on a rotating evaporator. A second solution was prepared by dissolving 4.43 g. (0.01 moles) of the dry lead tetraacetate in methylene chloride and diluting to exactly 50 ml. (concentration: 0.2 moles/liter).

Test tube reactions were carried out using a series of ratios of reactants and the samples were treated in the following manner: The lead tetraacetate solution was transferred to an 8 in. test tube with a pipet. Contact of the solution with air was kept to a minimum and the equipment was thoroughly dried. The hydrazone solution was added from a pipet and the stoppered test

tube was shaken for five minutes. Ten ml. of water was added and again the test tube was shaken. Any excess lead tetraacetate was converted to lead dioxide which was retained in the methylene chloride (bottom) layer. The addition of 25 ml. of diethyl ether inverted the water and organic layers, and the lead dioxide changed from organic to aqueous layer. The ether-methylene chloride layer was decanted, the water suspension of the lead dioxide was transferred to a centrifuge tube, and the lead dioxide was collected by centrifugation. After decanting the water, the lead dioxide was stirred with 5 ml. of ethanol, centrifuged, and the amounts of lead dioxide obtained for the different ratios of reactants were compared visually.

With mole ratios of lead tetraacetate to hydrazone of 1.8:1 and lower, no lead dioxide was formed. A trace amount of lead dioxide was found with a ratio of 2:1, and considerable amounts were obtained when the ratios were increased to 2.2:1 and 2.4:1. The increase in lead dioxide obtained paralleled the increase in lead tetraacetate solution used. From these observations the conclusion was drawn that lead tetraacetate reacts with the hydrazone in a ratio of 2:1.

2.) Reaction of Benzophenone-N,N-dimethylhydrazone with Lead Tetraacetate

A solution of 11.20 g. (0.05 moles) of benzophenone-N,N-dimethylhydrazone in 50 ml. of methylene chloride was added dropwise to a stirred solution of 55.40 g. (0.125 moles) of lead tetraacetate. The reaction is somewhat exothermic and the temperature of the reaction mixture was maintained between 0 and 5° by immersing the reaction flask in an ice-water bath. After a few ml. of the hydrazone solution had been added, turbidity and a yellow color developed. Toward the end of the addition a gummy, orange-colored substance

formed which changed on further stirring to a flaky, white precipitate of lead diacetate. The reaction mixture was stirred at room temperature for an additional 20-30 min. before 250 ml. of water was added. Any lead dioxide formed from unchanged lead tetraacetate was removed by filtration through a celite mat.* The methylene chloride layer was separated, washed first with water, then twice with saturated sodium bicarbonate solution to remove any acetic acid, once more with water and then dried over anhydrous sodium sulfate. After removing the major portion of solvent by distillation, the remaining solvent was evaporated, leaving 14.00 g. of yellow solid. Two recrystallizations from petroleum ether (60-110°) yielded 10.00 g. of pale yellow crystals, m.p. 126-127°. The ultraviolet absorption spectrum showed a maximum at 345 mμ, log ϵ 1.86. The compound was identified as α -acetoxy- α -methylazodiphenylmethane. [Literature values: m.p. 125-126°, λ_{\max} 352 mμ, log ϵ 1.58 (13)]. Analysis, calculated for $C_{16}H_{16}N_2O_2$: C, 71.60; H, 6.01; N, 10.44. Found: C, 70.29; H, 6.04; N, 10.84. Mixed melting point with an authentic sample of the compound, prepared by Iffland, Salisbury and Schafer (13) showed no depression. The infrared spectra of the reaction product and the authentic sample of the azoacetate were found to be identical. The reaction was repeated twice and 60-75% yields of azoacetate were obtained.

Investigation of the aqueous portion of the reaction mixture showed that a positive Tollens' Test could be obtained. The water layer was distilled and approximately 100 ml. of distillate was collected. Treatment

* To avoid the often troublesome filtration, especially when a large amount of lead dioxide is present, 250 ml. of diethyl ether may be added. The lead dioxide remains in the water layer (bottom) and the organic layer can be decanted easily.

of this distillate with 2,4-dinitrophenylhydrazine reagent produced a yellow precipitate which, after several recrystallizations from ethanol, melted at 163-164°. It was identified as formaldehyde-2,4-dinitrophenylhydrazone. [Literature value: m.p. 166° (19)]. Mixed melting point with an authentic sample (m.p. 163-164°) showed no depression.

The reaction was repeated with 0.45 g. (0.002 moles) of the hydrazone and 2.23 g. (0.005 moles) of lead tetraacetate in a total of 40 ml. of glacial acetic acid as solvent. The slightly exothermic reaction produced no color change or turbidity. The reaction mixture was allowed to stand for ca. 45 min. and then diluted with 150 ml. of water. All organic products were extracted into a total of 200 ml. of diethyl ether, and the ether extract was washed with 50-ml. portions of water and saturated sodium bicarbonate solution until all acetic acid had been removed. After drying the diethyl ether solution with anhydrous sodium sulfate, the solvent was evaporated, leaving 0.51 g. of yellow crystals. The infrared spectrum of the crude reaction product is extremely similar to the spectrum of α -acetoxy- α -methylazodiphenylmethane. A slight N-H band at 3300 cm^{-1} suggests the presence of a trace of benzophenonemethylhydrazone. The impure crystals were recrystallized from petroleum ether (60-110°) and 0.30 g. (56% of theory) of α -acetoxy- α -methylazodiphenylmethane was obtained and identified by the method of mixed melting point. The presence of formaldehyde in the water layer was demonstrated by a positive Tollens' Test.

3.) Reaction of Benzophenone-N-methyl-N-phenylhydrazone with Lead Tetraacetate

a.) Normal addition

A solution of 4.29 g. (0.015 moles) of benzophenone-N-methyl-N-phenylhydrazone in methylene chloride was added to 16.83 g. (0.038 moles) of lead tetraacetate dissolved in methylene chloride according to the procedure

outlined for the dimethyl compound. The reaction proceeded identically except that a yellow-brown oil was obtained after removal of the solvent. When a seed crystal of α -acetoxy- α -phenylazodiphenylmethane was introduced, the oil solidified, and after recrystallization from petroleum ether (60-110°) 2.74 g. of bright yellow crystals were isolated, m.p. 97-100°. They were identified as α -acetoxy- α -phenylazodiphenylmethane. A mixed melting point with an authentic sample of the compound indicated no depression. The ultraviolet spectrum (Fig. 1) shows maxima at 272 m μ , log ϵ 4.14 and 395-402 m μ , log ϵ 2.47 which correspond to those of α -acetoxy- α -phenylazodiphenylmethane prepared by Iffland, Salisbury and Schafer (13). [Literature values: m.p. 101-103°, λ_{\max} 269 m μ , log ϵ 4.14; λ_{\max} 400 m μ , not measured]. The compound was obtained in 56% yield.

The presence of formaldehyde in the water layer as one of the reaction products was confirmed by Tollens' Test and formation of the 2,4-dinitrophenylhydrazine derivative (m.p. 163-164°) as outlined in the previous section.

Since benzophenonephenylhydrazone was only later identified as one of the products in the reaction of benzophenone-N-ethyl-N-phenylhydrazone with lead tetraacetate (see paragraph 5), a search for this compound was not made at the time the reaction, described above, was first carried out. Therefore, the reaction was repeated on a small scale (0.15 g., 0.0005 moles of hydrazone and 0.46 g., 0.00125 moles of lead tetraacetate). The reaction was contained in a centrifuge tube; lead dioxide and liquid were separated by centrifugation and decanting. The methylene chloride layer was washed and dried as previously outlined and the solvent evaporated. Examination of the ultraviolet spectrum of the crude reaction mixture confirmed the presence of benzophenonephenylhydrazone. A maximum was observed at 340 m μ (characteristic of benzophenonephenylhydrazone) where the absorption of the azoacetate is insignificant (Fig. 1 and 2).

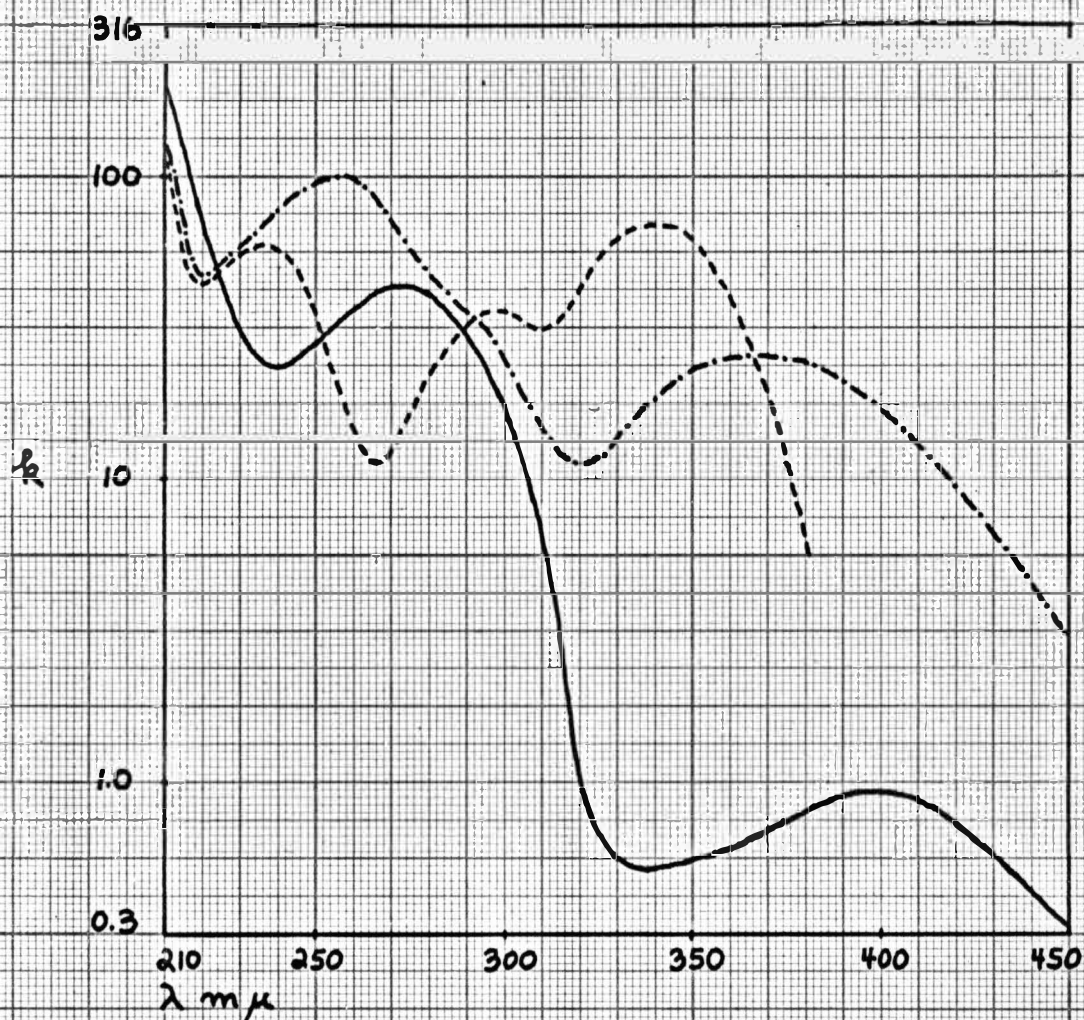


FIG. 1

- α -ACETOXY- α -PHENYLAZODIPHENYL-METHANE
- BENZOPHENONEPHENYLHYDRAZONE
- · - · - BENZOPHENONE-N-METHYL-N-PHENYLHYDRAZONE

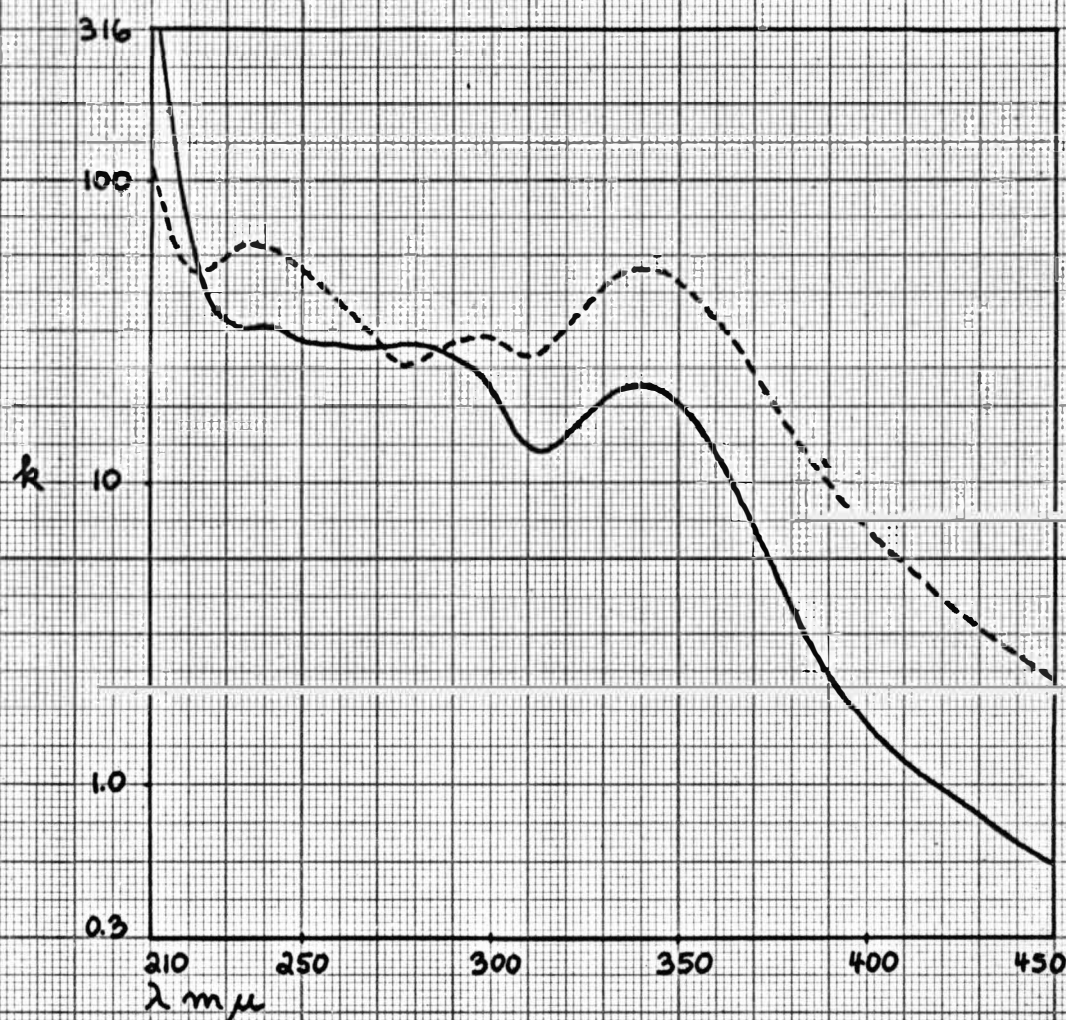


FIG. 2

- REACTION PRODUCT OF BENZOPHENONE-
N-METHYL-N-PHENYLHYDRAZONE WITH
LEAD TETRAACETATE, NORMAL ADDITION
- REACTION PRODUCT OF BENZOPHENONE-
N-METHYL-N-PHENYLHYDRAZONE WITH
LEAD TETRAACETATE, REVERSE ADDITION

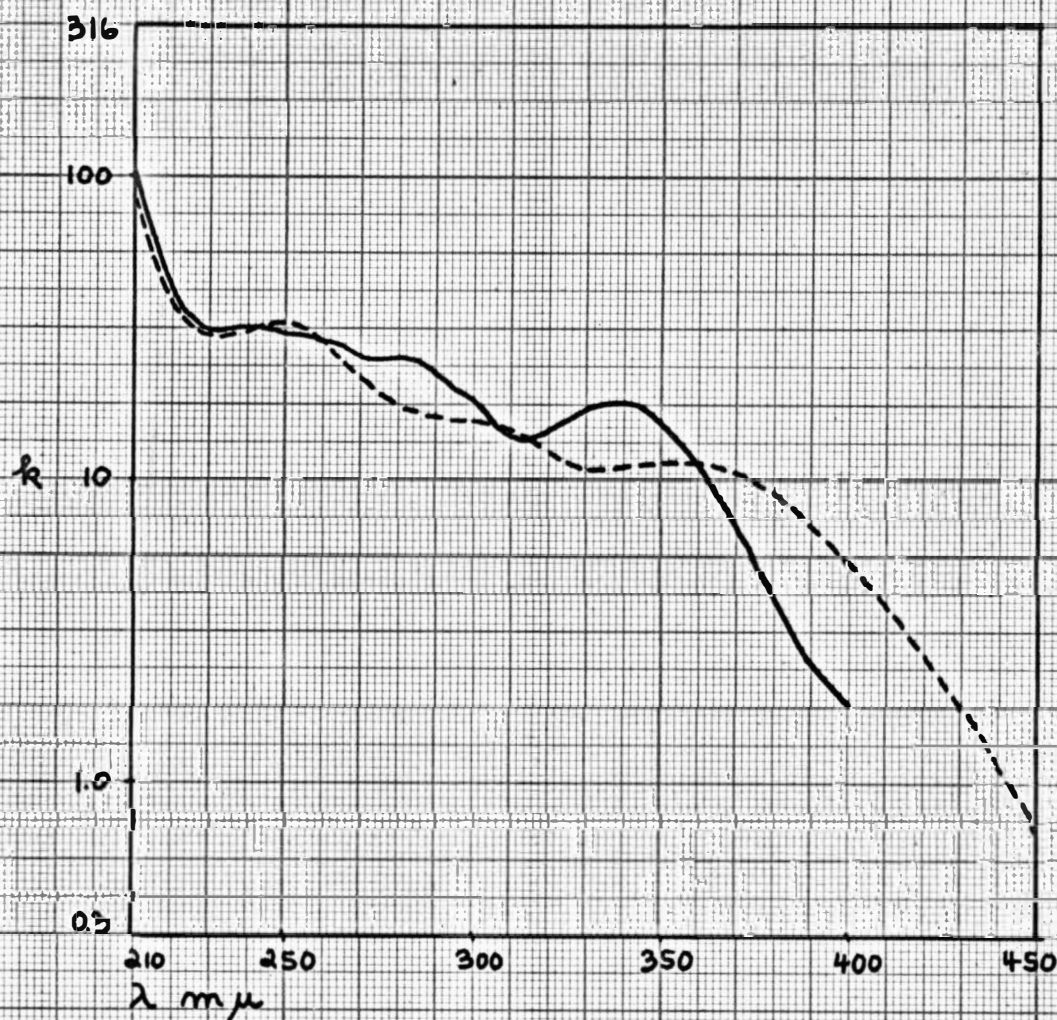


FIG. 3

————— REACTION PRODUCT OF BENZOPHENONE-
N-ETHYL-N-PHENYLHYDRAZONE WITH
LEAD TETRAACETATE

----- REACTION PRODUCT OF BENZOPHENONE-
N,N-DIPHENYLHYDRAZONE WITH LEAD
TETRAACETATE

b.) Reverse addition, approximate 1:1 ratio of reactants

A solution of 8.39 g. (0.018 moles) of lead tetraacetate in 60 ml. of methylene chloride was added to a cooled, stirred solution of 5.72 g. (0.02 moles) of benzophenone-N-methyl-N-phenylhydrazone in 50 ml. of methylene chloride over a period of 1 1/2 hrs., keeping the temperature between 0 and 5°. Turbidity developed almost immediately, followed by the formation of a white precipitate. The gummy material observed in all previously described reactions did not form. After stirring the reaction mixture at room temperature for one hour, solvent and all volatile products were evaporated under reduced pressure and condensed in a trap, cooled by a dry-ice-trichloroethylene mixture. Since the condensate gave a positive Tollens' Test, it was examined for formaldehyde. Extraction with water and treatment of the extract with 2,4-dinitrophenylhydrazine reagent gave a yellow 2,4-dinitrophenylhydrazine derivative. Since, after several recrystallizations from ethanol, a satisfactory melting point could not be obtained (m.p. range 103-120°), the infrared spectrum of the derivative was used for identification. The spectrum proved to be identical to that of authentic formaldehyde-2,4-dinitrophenylhydrazone (m.p. 163-164°).

The residue left after removal of volatile material was washed with benzene to separate organic compounds from lead diacetate. To remove acetic acid, the benzene solution was chromatographed on a neutral alumina column (Fisher Scientific Company #A540). The light brown, acid-free eluate was concentrated and again chromatographed on neutral alumina. Eluting with benzene, twenty fractions (volumes ca. 2-3 ml.) were collected. On evaporation of the solvent, fractions 1-7 crystallized in part, fractions 8-11 produced an orange-brown oil, fractions 12-20 traces of brown oil, and a dark band was finally eluted with methanol. The ultraviolet spectrum of fraction two resembled that of benzophenonephenylhydrazone with only slight

irregularities and, using the maximum at 340 mμ (as previously described), the benzophenonephenylhydrazone content of fraction two was calculated to be approximately 72% (Fig. 2). A shoulder at 260 mμ is probably due to the presence of unchanged starting hydrazone (Fig. 1). Ultraviolet absorption of fraction nine indicates the presence of benzophenonephenylhydrazone (maxima at 340 and 240 mμ), but the increased absorption at 260 mμ resulting in a more pronounced shoulder indicates a large percentage of starting hydrazone.* Neither of the two curves gives any indication of the presence of the expected azoacetate (Fig. 1).

4.) Reaction of Benzophenone-N-ethyl-N-phenylhydrazone with Lead Tetraacetate

The reaction was conducted with 3.00 g. (0.01 moles) of the hydrazone and 10.50 g. (0.0225 moles) of lead tetraacetate in a total of 150 ml. of methylene chloride using the standard procedure and showed behavior analogous to that involving the dimethyl compound. After removal of the solvent, 3.88 g. of an orange-brown, viscous residue was isolated. Cooling, stirring and seeding with α-acetoxy-α-phenylazodiphenylmethane did not induce crystallization. Since the ultraviolet spectrum of the residue had the characteristics of that of a mixture (Fig. 3), a separation by column chromatography was attempted. A portion of the residue, 2.12 g., was dissolved in benzene, passed through a neutral alumina column (13 mm., 35 cm.) and a total of twenty five fractions (volumes ca. 2-3 ml.) were eluted with benzene. A dark brown band was

* A trial separation of a synthetic mixture of benzophenonephenylhydrazone and benzophenone-N-methyl-N-phenylhydrazone on neutral and basic alumina demonstrated that both adsorbents give only partial and poor separation. Recrystallization from petroleum ether favors the concentration of benzophenonephenylhydrazone while the second component tends to stay in solution.

eluted with methanol. Fractions 1-7 crystallized after the solvent was evaporated; the remaining fractions contained only traces of brown oil. Fractions 1 and 2, on recrystallization from petroleum ether (60-110°), gave light tan needles, m.p. 134-137°, and the compound was identified as benzophenonephenylhydrazone. [Literature value: m.p. 137-138° (11)]. Mixed melting point with the authentic compound gave no depression. Furthermore, the infrared and ultraviolet spectra of the reaction product were identical to those of benzophenonephenylhydrazone. Fractions 5-7, on recrystallization, yielded bright yellow crystals, m.p. 98-100°, which were identified as α -acetoxy- α -phenylazodiphenylmethane by the method of mixed melting points and ultraviolet spectra, previously discussed for the benzophenone-N-methyl-N-phenylhydrazone reaction. Fractions 3 and 4 showed melting point depressions and were presumably a mixture of the two identified compounds. A necessarily approximate calculation, based on the weight of fractions 1 and 2 for benzophenonephenylhydrazone and fractions 3-7 for the azoacetate, indicated that minimum yields for these compounds were 20 and 50% respectively (based on the starting hydrazone).

Acetaldehyde was found in the aqueous portion of the reaction mixture and the 2,4-dinitrophenylhydrazine derivative was prepared which, after several recrystallizations, gave a m.p. and mixed m.p. 155-159° and 154-158° respectively, the difficulties possibly being due to geometric isomerism. [Literature values: m.p. 168°, stable; m.p. 157°, unstable; m.p. mixture 148° (11)].

5.) Reaction of Benzophenone-N,N-diphenylhydrazone with Lead Tetraacetate

By first carrying out the reaction on a small scale (0.0005 moles of hydrazone and 0.00125 moles of lead tetraacetate), it was established that a reaction does take place. The reaction mixture darkened on mixing

but failed to develop turbidity. A small amount of lead diacetate precipitated after a period of one hour and more precipitate formed when the reaction mixture was allowed to stand overnight. Addition of water did not produce the usual lead dioxide. A brown-black residue was obtained following the standard isolation procedure.

The infrared spectrum showed an acetate band (1760 cm^{-1}) but no N-H band in the $3200\text{-}3400\text{ cm}^{-1}$ region and, therefore, no benzophenonephenylhydrazone was formed in this reaction.

In the ultraviolet spectrum of the residue (Fig. 3), maxima were located at 248 and 352 m μ with a shoulder at ca. 300 m μ , which does not correspond to the maxima characteristic of an aromatic N-substituted azoacetate (13).

The water layer failed to give a positive Tollens' Test.

The reaction was repeated using 0.70 g. (0.002 moles) of the hydrazone and 4.66 g. (0.01 moles) of lead tetraacetate and, at the end of the reaction time when water was added, a considerable amount of lead dioxide was obtained. The ultraviolet absorption curve of the residue was similar to that plotted for the previous reaction, with maxima located at 250 and 348 m μ . In the infrared spectrum the residue again produced acetate absorption at 1760 and 1230 cm^{-1} .

Purification and/or separation of the residue was attempted by chromatographing the benzene solution of the residue on neutral alumina. After evaporation of the benzene, fractions 1-7 produced a light green oil, fractions 9-15 a yellow-brown oil. A large, dark band was eluted with methanol.

Fraction 5, representative of the first-eluted component, was examined and showed ultraviolet absorption maxima at 252-255 and 351 (broad) m μ . The infrared spectrum of this fraction exhibited the following bands not present

in the spectrum of the starting material: 3 bands in the $2840\text{-}2940\text{ cm}^{-1}$ region (aliphatic C-H bonds), 1758 cm^{-1} (possibly acetate absorption), 1725 , 1663 , 1370 , 1230 and 1120 cm^{-1} . Fraction 11, representative of the later eluted component, showed ultraviolet absorption maxima at 256 and $360\text{ m}\mu$. New bands in the infrared spectrum, which were not present in the starting material, are: $2830\text{-}2925\text{ cm}^{-1}$ (aliphatic C-H bonds), 1755 cm^{-1} (possibly acetate absorption), 1720 , 1660 , 1640 , 1550 and 1370 cm^{-1} .

Neither component was identified.

6.) Reaction of Acetone-N-methyl-N-phenylhydrazone with Lead Tetraacetate

The usual procedure was followed in the reaction of 8.10 g. (0.05 moles) of acetone-N-methyl-N-phenylhydrazone with 48.80 g. (0.11 moles) of lead tetraacetate in a total of 300 ml. of methylene chloride as solvent. All of the lead tetraacetate reacted, since no lead dioxide formed with the addition of water. The residue obtained after evaporation of the solvent, a light brown oil, decomposed during the attempted distillation at reduced pressure to a black, tarry substance.

Formaldehyde was found present in the water layer and was identified by its 2,4-dinitrophenylhydrazine derivative (m.p. $164\text{-}166^{\circ}$).

The reaction was repeated on a small scale using a ratio of hydrazone to lead tetraacetate of $1\text{:}2.5$, and still no lead dioxide formed when water was added. The infrared spectrum of the reaction product was compared to that of the expected azoacetate (2-acetoxy-2-phenylazopropane). An N-H band (3305 cm^{-1}) was found which is not present in the spectrum of the azoacetate. On the other hand, several azoacetate bands (1530 , 1483 , 935 , 867 , 835 cm^{-1}) were missing in the spectrum of the reaction product and several bands (1582 , 760 cm^{-1}) seemed to be displaced. A new band appeared at 1505 cm^{-1} .

A reaction with ratio 4:1 of lead tetraacetate to hydrazone was tried next, and this time lead tetraacetate was in excess. Again examining the infrared spectrum of the reaction product, all azoacetate bands could be located, although one band at 1483 cm^{-1} seemed to be slightly displaced.

7.) Reaction of Benzophenonephenylhydrazone with Lead Tetraacetate in the Presence of Ethylidenediacetate

Ethylidenediacetate was prepared by the method of Davey and Gwilt (6), b.p. $62-64^{\circ}$ at 10 mm., $n_D^{24.5}$ 1.3990-1.3992. [Literature value: b.p. $54-55^{\circ}$ at 10 mm. (15)].

A solution of 1.46 g. (0.01 moles) of ethylidenediacetate and 1.36 g. (0.005 moles) of benzophenonephenylhydrazone in 10 ml. of methylene chloride was prepared and slowly added to a solution of 4.43 g. (0.01 moles) of lead tetraacetate in 15 ml. of methylene chloride, cooled in an ice-water bath. The reaction behavior was typical of a hydrazone-lead tetraacetate reaction. After allowing the reaction mixture to stand for ca. one hr., 6 ml. of solvent (b.p. up to 38°) was removed by distillation through a fractionating column (1.5 x 30 cm.). The distillate slowly deposited a silver mirror in the Tollens' Test. However, a carbonyl band was not observed in the $1700-1750\text{ cm}^{-1}$ region of the infrared spectrum of the solution.

C. Reaction of Dimethylaniline with Lead Tetraacetate

A solution of 1.20 g. (0.01 moles) of redistilled dimethylaniline (b.p. 51.5° at 3 mm., n_D^{26} 1.5556) in 10 ml. of methylene chloride was prepared and the amine salt formed by addition of 0.60 g. (0.01 moles) of glacial acetic acid. This solution was slowly added to a solution of 11.10 g. (0.025 moles) of lead tetraacetate in 30 ml. of methylene chloride. A fleeting green-blue color was observed on contact of drops; turbidity developed and gummy material

formed which later changed to a white precipitate (lead diacetate) suspended in a light brown solution. The reaction was exothermic and the temperature of the solution rose to 38° during the addition.

The addition of 60 ml. of water produced a dark brown organic, and a wine red aqueous layer but no trace of lead dioxide. The methylene chloride layer was successively washed with water, saturated sodium bicarbonate solution and water and was dried over anhydrous sodium sulfate. Gas-liquid chromatography of the methylene chloride solution confirmed the absence of unchanged dimethylaniline. Evaporation of the solvent produced a dark brown, viscous oil.

The infrared spectrum of this residue shows several new absorption bands ($3300, 1750, 1675, 1370, 932, 917 \text{ cm}^{-1}$) not present in the spectrum of the starting material; otherwise the spectra are similar. Several peaks characteristic of the amine ($2780, 1347, 1062, 945, 860, 805 \text{ cm}^{-1}$) could not be found in the spectrum of the product.

The reaction was repeated increasing the amount of lead tetraacetate to 22.20 g. (0.05 moles). The amount of lead diacetate which precipitated was considerably increased and the addition of water produced lead dioxide which was filtered. The organic layer was treated as previously described and 1.43 g. of dark brown, viscous residue was isolated.

The residue was subjected to acid-catalyzed hydrolysis for 20 hrs., using an ethanol-water mixture as solvent. The initially acidic hydrolysis mixture was steam-distilled, made basic with sodium hydroxide, and the steam distillation was continued. The distillate from the basic hydrolysis mixture had the odor of an amine and its vapors tested alkaline with moist litmus paper. The Hinsberg Test produced traces of insoluble white solid, suggesting the presence of a secondary amine which was not identified.

D. Reactions of Hydrazones with Manganese Dioxide and Acetic Acid

1.) Reaction of Acetonephenylhydrazone with Manganese Dioxide and Acetic Acid

The method of Henbest and Thomas (10) developed for oxidation of N-alkyl- and N,N-dialkylanilines with manganese dioxide was adapted and applied to hydrazones.

The reaction mixture, prepared by addition of 150 g. of manganese dioxide (Matheson, Coleman and Bell, CB501, technical, powder), 3.00 g. (0.02 moles) of acetonephenylhydrazone and 2.40 g. (0.04 moles) of glacial acetic acid to 300 ml. of chloroform, was stirred at room temperature for 24 hrs.

After filtering the manganese dioxide, the reddish-brown chloroform solution was washed successively with portions of water, saturated sodium bicarbonate solution and water and was dried with anhydrous sodium sulfate. The solvent was distilled and the last traces evaporated under vacuum, leaving a dark brown, viscous residue.

The infrared spectrum of the residue does not exhibit any carbonyl absorption in the region of $1730\text{--}1800\text{ cm}^{-1}$, thus no azoacetate was produced in the reaction. Bands at 3315, 1318, 1270, 1250, 1125, 1037, 995, 880 cm^{-1} , characteristic of the starting material, were missing in the spectrum of the reaction product(s) which showed newly developed bands at 1220, 850 and 770 cm^{-1} . No identification of the product(s) was made.

2.) Reaction of Benzophenone-N-methyl-N-phenylhydrazone with Manganese Dioxide and Acetic Acid

The same procedure as for the acetonephenylhydrazone was followed, using 57.0 g. of manganese dioxide, 1.14 g. (0.004 moles) of the hydrazone and 2.40 g.

(0.04 moles) of glacial acetic acid in 100 ml. of chloroform. The infrared spectrum of the isolated reaction product(s) was compared with the spectrum of the starting hydrazone, and bands at 2780, 1421 and 873 cm^{-1} , characteristic of the hydrazone, could not be located in the spectrum of the reaction product. On the other hand, the latter showed newly developed bands at 2950, 1747, 1712, 1660, 1370 and 1348 cm^{-1} , clearly indicating that a reaction did occur. When comparing the spectrum of the reaction mixture to that of the expected azoacetate, all bands of the azoacetate spectrum were found to be present in the spectrum of the reaction product, but additional bands at 2950, 1712, 1660, 1393, 1348, 1320, 1280, 1095, 1070, and 940 cm^{-1} were also found. Thus, the azoacetate and other unidentified products appear to be formed in this reaction.

E. Reactions of Ketohydrazones with Benzoyl Peroxide

1.) Reaction of Benzophenonephenylhydrazone with Benzoyl Peroxide

A solution of 1.41 g. (0.005 moles) of benzophenonephenylhydrazone in 15 ml. of methylene chloride was added slowly to a solution of 2.42 g. (0.01 moles) of benzoyl peroxide in 10 ml. of methylene chloride. The reaction mixture darkened immediately and the temperature rose to 35° during the mixing.

Successive treatment of the reaction mixture with 50-ml. portions of water and saturated sodium bicarbonate solution removed all benzoic acid formed. The methylene chloride solution was dried with anhydrous sodium sulfate, and the solvent was evaporated. A dark brown oil, containing observable crystals, was obtained and slowly decomposed at room temperature. A portion of the crude oil was dissolved in ethanol, and, upon cooling, yielded crystals, m.p. $95-100^{\circ}$ (decomposition) which were identified as unchanged benzoyl peroxide.

The filtrate, on standing, produced an additional amount of yellow crystals, m.p. 140-143° (decomposition). The infrared spectrum of this second crop of crystals was compared with that of α -benzoxy- α -phenylazodiphenylmethane (m.p. 149-152°) [Literature value: m.p. 159-161° (13)] and exhibited all absorption bands of the azobenzoate besides additional bands at 1765, 1717, 1364 and 1222 cm^{-1} .

2.) Reaction of Benzophenone-N-methyl-N-phenylhydrazone with Benzoyl Peroxide

The reaction described in section 1 was repeated with 1.43 g. (0.005 moles) of benzophenone-N-methyl-N-phenylhydrazone and 4.85 g. (0.02 moles) of benzoyl peroxide in a total of 50 ml. of methylene chloride. The reaction proceeded somewhat slower as evidenced by the gradual darkening of the reaction mixture. A dark brown, viscous oil (4.52 g.) was isolated which contained some crystalline material. Washing with cold ethanol removed the oil from the crystals, which were recrystallized from ethanol and identified as benzoyl peroxide, m.p. 104-107°. [Literature value m.p. 108° (d.) (14)].

The solvent was evaporated from the oil-ethanol solution; the oil was re-dissolved in benzene, and the solution chromatographed on neutral alumina, collecting twelve fractions (volumes ca. 2-3 ml.). Fraction 3, which solidified in part, was recrystallized from ethanol, yielding yellow crystals, m.p. 138-142°. They were identified as α -benzoxy- α -phenylazodiphenylmethane by their infrared spectrum, which proved to be identical to that of an authentic sample of the compound.

DISCUSSION OF EXPERIMENTAL RESULTS

A. Reactions of N,N-disubstituted Ketohydrazones with Lead Tetraacetate1.) Stoichiometry of the Reaction

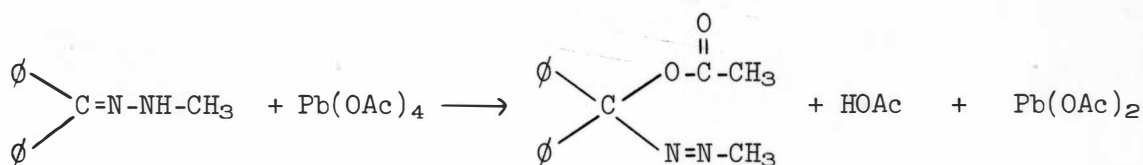
In contrast to the reaction of lead tetraacetate with N-monosubstituted ketohydrazones, which was observed by Iffland, Salisbury and Schafer (13) to have a stoichiometry of 1:1, the reaction of lead tetraacetate with N,N-disubstituted ketohydrazones appeared to have different stoichiometric requirements. When using the reagents in a ratio of 1:1, difficulties in isolating and identifying reaction products were encountered, and it was observed that no lead dioxide formed after addition of water to the reaction mixture. This indicated the complete consumption of lead tetraacetate in the reaction and suggested the need of a higher ratio of lead tetraacetate to hydrazone.

By carrying out a series of small-scale reactions using standard solutions, the lowest ratio of lead tetraacetate to hydrazone for which the first trace of lead dioxide was detected, was found to be 2:1. As the ratio was further increased, the amount of lead dioxide formed, increased in a parallel manner. These observations conclusively established that two molecules of lead tetraacetate are consumed in the reaction for each molecule of N,N-disubstituted hydrazone. Accordingly, a ratio of 2.25:1 of lead tetraacetate to hydrazone was generally used in carrying out these reactions, unless otherwise specified.

2.) Reaction of Benzophenone-N,N-dimethylhydrazone with Lead Tetraacetate

When the reaction was carried out for the first time using a 1:1 ratio of reactants, a yellow oil was isolated which was unstable and decomposed slowly at room temperature with evolution of gas. When a ratio of 2:1 (lead tetraacetate to hydrazone) was used, no isolation problems were encountered. A pale yellow,

crystalline solid formed on evaporation of the solvent and was easily purified by recrystallization from petroleum ether. It was identified as α -acetoxy- α -methylazodiphenylmethane, which had previously been prepared by the reaction of benzophenonemethylhydrazone with lead tetraacetate (13). For that reaction a radical type mechanism was proposed which involved the removal of the hydrogen atom attached to the nitrogen atom by an acetate radical to form acetic acid, and the formation of a resonance hybrid that was converted to an azoacetate by the addition of a second acetate radical to the carbonyl carbon. The overall reaction can be expressed by the following equation:



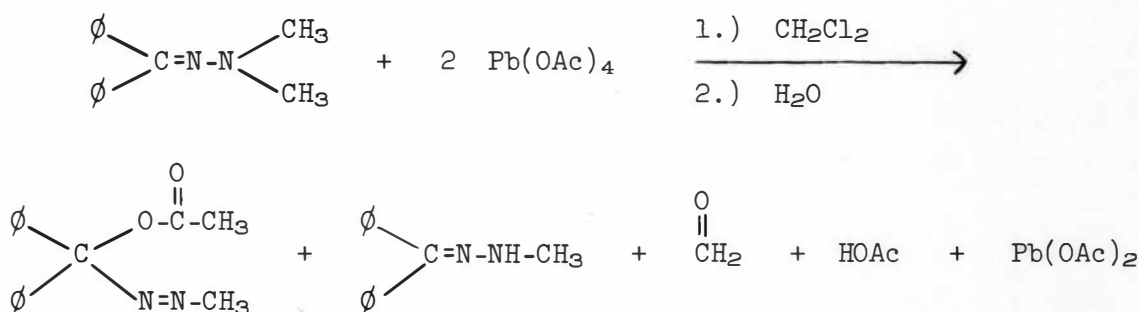
To obtain the same azoacetate from benzophenone-N,N-dimethylhydrazone, one of the methyl groups must be removed by breaking of a C-N bond, and a similar rearrangement must take place as described for the benzophenonemethylhydrazone. The methyl group is ultimately converted to formaldehyde and was identified by its 2,4-dinitrophenylhydrazine derivative.

Since, from the results obtained in later experiments (see section 3), the presence of benzophenonemethylhydrazone in the reaction mixture could be expected,* the reaction was repeated and the crude reaction mixture was examined for the

* The fact that the crude product, obtained when a 1:1 ratio of reactants was used, decomposed slowly, also supports this expectation, since the compound is known to be unstable and is later proposed as a reaction intermediate whose concentration would be favored by a 1:1 ratio of reactants.

presence of benzophenonemethylhydrazone. Since the compound, an unstable liquid (13), was not available as reference, an N-H band at 3300 cm^{-1} in the infrared spectrum of the reaction mixture was taken as evidence for its presence (at least in a small amount) in the reaction mixture, supported by the fact that analogous N-monosubstituted hydrazones were obtained and positively identified in similar reactions, described later.

From the identification of products, the following incomplete and unbalanced equation can be written for the reaction:



Obviously, the mechanism proposed for the reaction of benzophenonemethylhydrazone does not fit this reaction, because it does not explain the consumption of two molecules of lead tetraacetate.

3.) Reaction of Benzophenone-N-alkyl-N-arylhydrazones with Lead Tetraacetate

The reactions of two compounds of this type, benzophenone-N-methyl-N-phenylhydrazone and benzophenone-N-ethyl-N-phenylhydrazone with lead tetraacetate, were investigated.

As was expected, the alkyl group was removed by cleavage of the C-N bond and converted to formaldehyde and acetaldehyde respectively, which were

identified as their 2,4-dinitrophenylhydrazine derivatives by mixed melting points with an authentic sample of the compound.

In the case of benzophenone-N-methyl-N-phenylhydrazone no difficulty was encountered in obtaining the expected azoacetate, α -acetoxy- α -phenylazodiphenylmethane. The isolated reaction product, a yellow-brown oil, solidified when seeded; the solid was recrystallized from petroleum ether and identified by a mixed melting point with a sample prepared by the reaction of benzophenone-phenylhydrazone with lead tetraacetate.

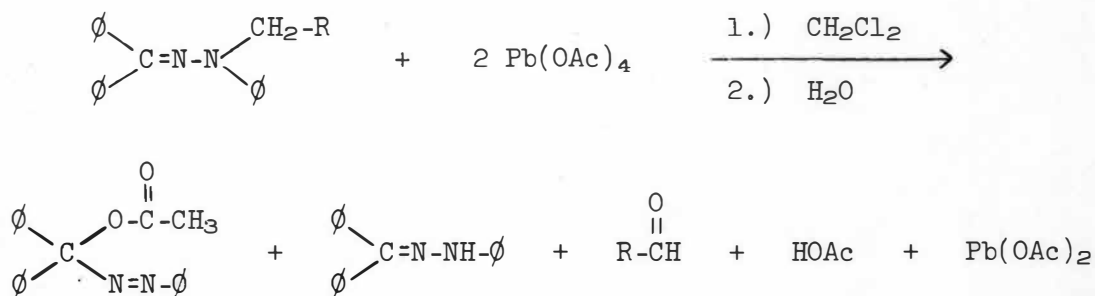
Repeating the reaction with benzophenone-N-ethyl-N-phenylhydrazone, the same azoacetate was expected to be produced, but the oily product did not solidify. The ultraviolet spectrum of the oil was characteristic of that of a mixture (Fig. 3), and a separation into two components was achieved by column chromatography on neutral alumina. The early-eluted fractions contained a compound identified as benzophenonephenylhydrazone by the method of mixed melting point and comparison of the infrared and ultraviolet spectra with those of an authentic sample of the compound.

Later fractions contained the expected α -acetoxy- α -phenylazodiphenylmethane. The yields of the two products were approximately 20 and 50% of theory respectively.

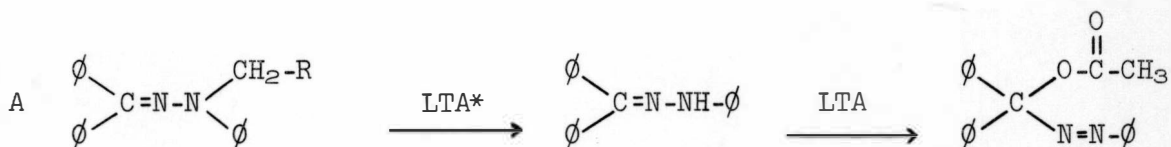
Since there was no particular reason to believe that the methyl compound should react differently than the ethyl compound, it was assumed that the benzophenonephenylhydrazone formed in the reaction of benzophenone-N-methyl-N-phenylhydrazone with lead tetraacetate had been lost in the recrystallization (as had been the case with benzophenone-N,N-dimethylhydrazone). To confirm the presence of benzophenonephenylhydrazone as one of the products, the reaction

was repeated on a small scale (0.0005 moles of hydrazone). Benzophenonephenylhydrazone was never isolated, but its presence was confirmed by the ultraviolet spectrum of the crude reaction product (Fig. 2) using the maximum at 340 mμ for benzophenonephenylhydrazone (Fig. 1) for identification which lies in a region of low absorption for the azoacetate (Fig. 1). This spectrum is extremely similar to that obtained from the crude reaction product (before chromatographing) of the ethyl compound with lead tetraacetate (Fig. 3). This was to be expected, since the products obtained are identical.

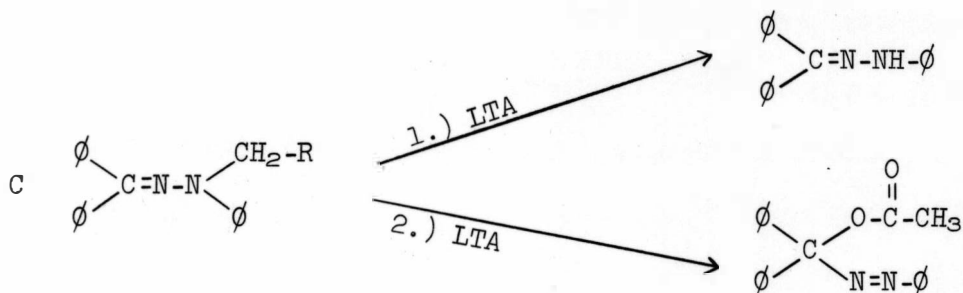
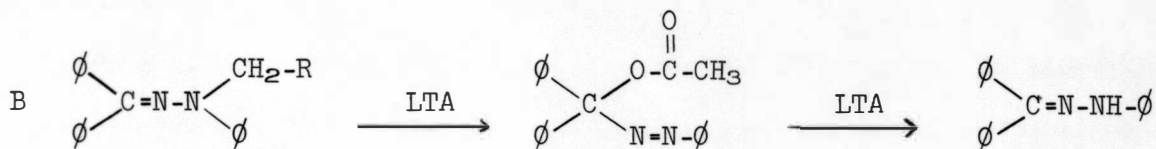
Thus, the following unbalanced, overall equation can be written for both analogous reactions, where R = H for the methyl compound and R = CH₃ for the ethyl compound:



Three different reaction paths to the reaction products may be considered. Sequences A and B involve consecutive reactions and path C involves competitive reactions:



* LTA abbreviation for lead tetraacetate



In an attempt to select the most reasonable of these three possibilities, the reaction of benzophenone-N-methyl-N-phenylhydrazone and lead tetraacetate was further examined. By a reverse order of addition (i.e. lead tetraacetate solution was added to hydrazone solution) and a ratio of 1:0.9 (hydrazone to lead tetraacetate), it was hoped to change the relative amounts of the products. In this way, either an increase, decrease or no change in the ratio of hydrazone to azoacetate would be expected if sequence A, B, or C respectively is the reaction path. The crude reaction product was chromatographed on neutral alumina, and the ultraviolet spectra of fraction 2 and 9 (representative of the early and late eluted component) examined.

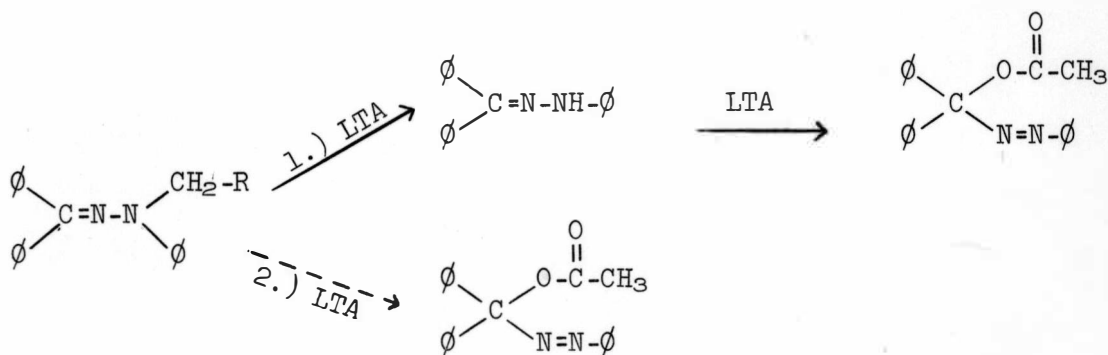
The spectrum of fraction 2 (Fig. 2) resembled that of benzophenonephenylhydrazone with a slight shoulder at 260 μ which is probably due to the presence of unchanged starting hydrazone (Fig. 1). The fraction consists of approximately 72% benzophenonephenylhydrazone calculated from the known ϵ at 340 μ .

Fraction 9 has a similar spectrum with the amount of starting hydrazone somewhat increased. No azoacetate could be detected in the reaction mixture.

From this observation, A appears to be the only acceptable reaction path, as the concentration of the intermediate product can be increased by reversing the order of addition; and the formation of the final product prevented, by use of a limited amount of lead tetraacetate. The path also accounts for the 2:1 stoichiometry of the reaction (providing that the first step is accomplished with a 1:1 ratio), and it has been established previously (13) that the second step takes place rapidly.

Path B must be ruled out since, under the above reaction conditions, a build-up of the concentration of azoacetate, rather than benzophenonephenylhydrazone, would be expected. Furthermore, it was demonstrated that the azoacetate does not react with lead tetraacetate. In this test the azoacetate was recovered and identified by its ultraviolet spectrum.

Path C is least likely because, as written, it does not readily account for the simple 2:1 stoichiometry of the reaction. Also, benzophenonephenylhydrazone further reacts with lead tetraacetate, and, therefore, one of the branches would have to be extended to a consecutive reaction as in A:

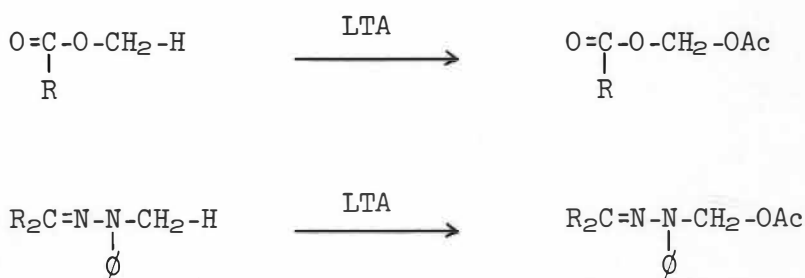


In order to rationalize the 2:1 stoichiometry, the bulk of the starting material would have to react via branch 1 which becomes essentially equivalent to Path A.

The reverse addition reaction was carried out and the products were isolated without the addition of water. Collection of solvent and other volatiles by vacuum evaporation provided a condensate that gave a positive Tollens' Test and the 2,4-dinitrophenylhydrazine derivative of formaldehyde. The infrared spectrum of the residue indicated the presence of the azoacetate. It must be concluded that there is formed either formaldehyde or a volatile formaldehyde precursor which decomposes to formaldehyde in the aqueous Tollens' Test or 2,4-dinitrophenylhydrazine test.

The oxidation of simple aliphatic esters by hot lead tetraacetate solution has been recently described by Mosher and Kehr (16). Carbon dioxide, methane and acetoxy esters (formed by reaction of the α -carbon atom in the alkyl portion of the ester) were the principle products and an ionic mechanism, involving a CH_3COO^+ [or $\text{Pb}(\text{OAc})_3^+$] intermediate, was presented to explain the reaction.

It has been noted that the C-H bond, oxidized in the Mosher reaction, is structurally equivalent to the C-H bond on the alkyl group removed in the reaction of lead tetraacetate with disubstituted hydrazones. Thus:



Although the lead tetraacetate-hydrazone reaction differs markedly from the Mosher reaction in temperature and in the absence of observed evolution of gases (carbon dioxide or methane), it is possible to speculate upon the

formation of an analogous ester intermediate (see above). It may be anticipated that this ester would further react, breaking the C-N bond and ultimately forming a diester such as methylene diacetate or ethylidene diacetate respectively from the methyl and ethyl derivatives. The facile decomposition of these gem-diesters to an aldehyde would not be surprising and would rationalize the formation of the observed aldehyde in the lead tetraacetate-hydrazone reactions.

In order to determine the reasonableness of this concept, ethylidene diacetate was introduced into a reaction mixture of lead tetraacetate and benzophenonephenylhydrazone. This was thought to approximate the composition of the byproducts in the reactions forming aldehydes. The mixture was then examined for acetaldehyde as indicated in the experimental section. A slow Tollens' Test was obtained on a methylene chloride distillate (b.p. up to 38°) of the reaction mixture; however, the presence of the carbonyl group could not be confirmed by infrared analysis.

In spite of the attractiveness of this relationship in the reactions of hydrazones and esters with lead tetraacetate, its validity remains inconclusive.

An alternate reaction path for the lead tetraacetate-disubstituted hydrazone reaction proceeding via radical intermediates ($\text{AcO}\cdot$ etc.) is conceivable, analogous to the sequence proposed for the reaction of monosubstituted hydrazones with lead tetraacetate (13). In relation to this mechanism, it was demonstrated that benzoyl peroxide, which invariably reacts by way of radical processes (20), formed an azobenzoate from both benzophenonephenylhydrazone and benzophenone-N-methyl-N-phenylhydrazone at room temperature in methylene chloride. Furthermore, the formation of azoacetates from hydrazones with hydrogen peroxide

in acetic acid has been implied (13). Thus, although a free radical type process has not been established conclusively, it appears at this time more reasonable than an ionic process.

4.) Reaction of Benzophenone-N,N-diphenylhydrazone with Lead Tetraacetate

In contrast to the reactions of N,N-dialkyl and N-alkyl-N-phenylhydrazones described in the preceding sections, the reaction of the N,N-diphenylhydrazone proceeds very slowly. The first traces of lead dioxide appeared only after a reaction time of an hour.

The reaction was carried out with two different ratios of reactants. At a ratio of 2.5:1 of lead tetraacetate to hydrazone, no lead dioxide developed upon addition of water; while at a ratio of 5:1, lead dioxide was formed. Therefore, a different stoichiometry must apply to this reaction. Removal of a phenyl group from the molecule could not produce a carbonyl compound, and indeed, none was found in the reaction mixture.

The formation of benzophenonephenylhydrazone and α -acetoxy- α -azophenyl-diphenylmethane might be anticipated if N-phenyl cleavage occurred. However, the presence of these compounds in the reaction product could not be confirmed from a study of the infrared and ultraviolet spectra (Fig. 3) of the reaction product.

Column chromatography failed to produce purification leading to identifiable products. Although an acetate group is incorporated in the molecule, as shown in the infrared spectrum (1760 and 1230 cm^{-1}), the product is not an azoacetate.

5.) Reaction of Acetone-N-methyl-N-phenylhydrazone with Lead Tetraacetate

The reaction was repeated twice using ratios of lead tetraacetate to hydrazone of 2.5:1 and 4:1 and proceeded identically to the reactions of the benzophenone derivatives previously described. Formaldehyde was identified in the aqueous layer as the 2,4-dinitrophenylhydrazine derivative. Instead of attempting to isolate the remaining reaction products, interpretation of the infrared spectrum of the crude reaction product was used for identification.

In the reaction mixture, employing the smaller ratio, an N-H band at 3305 cm^{-1} was identified and a correspondence of peaks, especially in the 800-1000 cm^{-1} region of the infrared spectrum, justifies the assumption that the product is mainly acetonephenylhydrazone and does not contain observable amounts of the azoacetate.

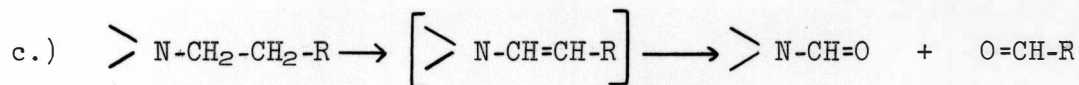
In the second reaction mixture, where the larger ratio was used, the N-H band at 3305 cm^{-1} is absent and the infrared spectrum contains all bands characteristic of the expected azoacetate, 2-acetoxy-2-azophenylpropane. In particular, the band at 935 cm^{-1} was observed, which has been tentatively assigned as a characteristic frequency of the skeleton -C=N=N-C- (2) and has been found present in all azoacetate spectra.

From this evidence it can be concluded that this reaction follows the same path as the reaction of the analogous benzophenone compound and the products produced are an azoacetate, acetonephenylhydrazone, formaldehyde, lead diacetate and acetic acid.

B. Reaction of Dimethylaniline with Lead Tetraacetate

Henbest and Thomas (9) have recently examined the reaction of N,N-dialkylanilines with manganese dioxide and have found that three different side chain

oxidations may occur, depending on the nature of the alkyl substituents:



Thus, dimethylaniline with manganese dioxide was converted to N-methyl-formanilide in 80% yield.

The possibility of accomplishing a similar side chain oxidation with lead tetraacetate was envisioned and tested by treating dimethylaniline with lead tetraacetate in ratios of 2.5:1 and 5:1 (lead tetraacetate to dimethylaniline), following the general procedure as outlined for the reaction of hydrazones with lead tetraacetate.

A reaction occurred as evidenced by a) the appearance of a fleeting blue color; b) rise in temperature and c) reduction of lead tetraacetate to lead diacetate. Changes in the infrared spectrum of the crude reaction product (a dark brown, viscous oil), were pronounced for both reactions, when compared to the spectrum of the dimethylaniline. The complete disappearance of the latter compound from the reaction mixture was demonstrated by gas-liquid chromatography. The stoichiometry of the reaction apparently lies between 2.5:1 and 5:1, since no unreacted lead tetraacetate was found in the first case, but addition of water produced lead dioxide in the second case.

No identification of the reaction products was completed but prolonged, acid-catalyzed hydrolysis of the crude reaction mixture and subsequent steam-distillation from alkali produced a small amount of material, which gave an insoluble solid in the Hinsberg Test, characteristic of a secondary amine.

Thus, the possibility that the lead tetraacetate oxidation proceeds via transformation a. analogous to the manganese dioxide oxidation is not eliminated. Hydrolysis of the N-methylformanilide would produce methylaniline, a secondary amine.

C. Reactions of Hydrazones with Manganese Dioxide in the Presence of
Acetic Acid

Because of the close similarity of the hydrazine portion of an N,N-disubstituted hydrazone to a tertiary amine, the manganese dioxide oxidation of N-alkyl and N,N-alkylanilines of Henbest and Thomas (10) was tried on both N-monosubstituted and N,N-disubstituted hydrazones in the presence of acetic acid, hoping to find an alternate oxidation of hydrazones that forms azoacetates.

Acetonephenylhydrazone and benzophenone-N-methyl-N-phenylhydrazone were treated with manganese dioxide in chloroform. Both reacted, as evidenced by changes in the infrared spectra of the crude reaction mixtures. No carbonyl absorption was found in the infrared spectrum of the reaction product from acetonephenylhydrazone, but all bands characteristic of the expected azoacetate could be located in the spectrum of the reaction product from the N,N-disubstituted hydrazone. Thus, the azoacetate is formed in the latter reaction, besides other unidentified products as evidenced by additional bands occurring in the spectrum.

SUMMARY

The reaction of lead tetraacetate with N,N-dialkyl and N-alkyl-N-aryl-ketohydrazone has been shown to have a 2:1 stoichiometry. The principle reaction product is an azoacetate analogous to that obtained from a monosubstituted ketohydrazone. The formation of a monosubstituted hydrazone has been established as an intermediate in the process, and the alkyl group is converted to an aldehyde. This new reaction has been compared to the lead tetraacetate oxidation of aliphatic esters and to the manganese dioxide oxidation of N,N-dialkylanilines. Consideration of mechanism has been inconclusive; however, a process involving free radical intermediates appears plausible and merits further examination.

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VITA

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She attended the Realgymnasium in Steyr and completed two semesters of studies at the University of Innsbruck, Austria. She came to the United States in June 1947 and was married to Otto J. Cerda in August 1947.

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APPROVAL OF EXAMINING COMMITTEE

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Don C. Offland
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Date

May 23 1961