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The Reaction of Metal Hydrides with Azoacetates

Thomas H. Althuis

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THE REACTION OF METAL HYDRIDES WITH AZOACETATES

by

Thomas H. Althuis

A thesis presented to the Faculty of the
School of Graduate Studies in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
October 1965

ACKNOWLEDGEMENT

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INTRODUCTION

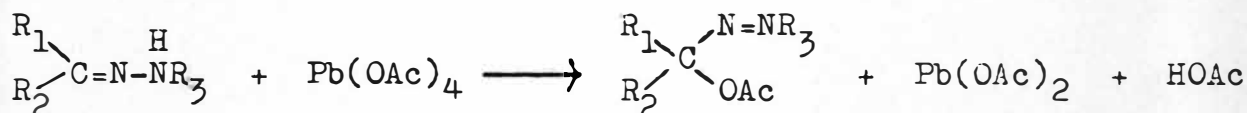
The term aliphatic azo compound refers to those azo compounds in which at least one of the two nitrogen atoms is linked to a tetrahedral, that is, sp^3 -hybridized carbon atom. Di-imides, $RN=NH$, however, are not being considered. Mixed aliphatic-aromatic azo compounds are those in which one nitrogen atom is linked to an sp^3 -hybridized carbon atom and the other to an aromatic sp^2 -hybridized carbon atom. If present, a symmetry element (point or plane) is determined by the mid-point between the two nitrogen atoms.

Unsymmetrical aliphatic azo compounds have been prepared only rarely. In the literature of 1929, Ramsperger¹⁷ reported the first synthesis of a simple mixed (unsymmetrical) aliphatic azo compound, 2-methylazopropane. This azo compound was prepared by oxidation of methylisopropylhydrazine with hydrogen peroxide to give only a 25% yield of the azo compound. The next compound of this type, which was reported in 1936, was 2-(isopropylazo)butane.² More recently Overberger and DiGiulio¹⁶ have synthesized a series of benzyl-azoalkanes: 2-(α -phenylethylazo)propane, 2-(α -cumylazo)propane, 3-(α,α -diethylbenzylazo)pentane, and 2-(α,α -methylisobutylbenzylazo)-4-methylpentane. These azo compounds were prepared by silver nitrate or mercuric oxide oxidation of their respective hydrazines which, except for the first, were pre-

pared by hydrogenation of the hydrazones.

The appearance of mixed aliphatic-aromatic azo compounds is much more frequent in the literature. As early as 1879 Fischer reported the synthesis of phenylazoethane⁸ followed by 1-phenylazo-2-propene⁹ in 1887. Since then these compounds and many others of the phenylazo- series have been reported numerous times. Some of these compounds include: phenylazomethane¹, phenylazopropane¹, 2-phenylazopropane^{1,15}, t-butylazobenzene¹⁵, phenylazopentane¹⁵, phenylazopentane¹, and phenylazocyclohexane¹⁵.

From the small number of unsymmetrical aliphatic azo compounds reported in the literature it is quite apparent that a successful method for preparing these compounds could open this virtually untouched area of organic chemistry. The method of oxidation of the related hydrazines has its limitations in that 1,2-dialkylhydrazines are quite rare.¹¹ Cerda⁷ has shown that an unsymmetrical azo compound could be obtained from the lithium aluminum hydride reduction of an azoacetate. It has been demonstrated that azoacetates can be prepared in good yields by the oxidation of keto-hydrazones with lead tetraacetate:¹³



Cerda⁷ first observed from vapor phase chromatographic data that 2-phenylazopropane was formed in 60% yield by the reaction of 2-acetoxy-2-phenylazopropane with lithium

aluminum hydride:



In view of this reaction, the reactions of other azoacetates with lithium aluminum hydride have been investigated.

EXPERIMENTAL

In the following experimental section all melting points and boiling points are expressed in degrees centigrade and are uncorrected. The ultraviolet spectra were measured with a Beckman Model DB recording spectrophotometer with the compounds dissolved in 95% ethanol. The infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer. Vapor phase chromatography was performed with either an Aerograph Gas Chromatograph Model A-90-C or an F&M Model 720 Dual Column Programmed Temperature Gas Chromatograph. A column packing using diethylene glycol succinate (DEGS) liquid phase was used. Galbraith Microanalytical Laboratories, Knoxville, Tennessee, performed the elemental analyses.

PREPARATION OF HYDRAZONES.

I. Preparation of acetone phenylhydrazone.-- This compound was prepared by the reaction of 108.0 g. (1.00 mole) of phenylhydrazine with 200 ml. (158 g., 2.73 moles) of acetone. After standing for several hours the solution was diluted with 500 ml. of water, extracted with ether, dried with anhydrous sodium sulfate, concentrated and vacuum distilled. The yellow distillate was collected in four portions having a total weight of 136 g. (92% yield) and the following range

of properties: b.p. 152-157° at 27 mm.; n_D^{25} 1.5848-1.5853. Literature value:³ n_D^{26} 1.585.

II. Preparation of cyclopentanone phenylhydrazone.--Equal molar amounts (0.18 moles) of cyclopentanone (14.7 g.) and phenylhydrazine (18.9 g.) were mixed and shaken with slight cooling. After 15 minutes the product solidified and was dissolved in 100 ml. of 30-60° petroleum ether. After separating the water, the organic layer was cooled and the crystalline product separated by filtration. Drying under vacuum gave 25.4 g. (84% yield) of pale yellow crystals: m.p. 51-52°. Literature value:¹⁸ m.p. 50°. Exposure of the hydrazone to the atmosphere causes noticable darkening and liquefaction within one hour.

III. Preparation of cyclohexanone phenylhydrazone.--Again equal molar amounts (0.50 moles) of cyclohexanone (49.1 g.) and phenylhydrazine (54.0 g.) were mixed and shaken until solid. The crude product was dissolved in 200 ml. of ethanol at 60° and water was added until turbid. Cooling and filtering yielded 84.0 g. (89% yield) of faintly orange needles: m.p. (after two hours) 69-76°. Literature value:¹⁵ m.p. 74-76°. Exposure to the atmosphere results in darkening and liquefaction.

IV. Preparation of acetone β -phenylethylhydrazone.--First, β -phenylethylhydrazine was prepared¹⁹ from 140 g. (1.00 mole) of β -phenylethylchloride and 96 g. (3.0 moles) of hydrazine. Distillation gave four portions of β -phenylethylhydrazine

totaling 67.5 g. (48% yield): b.p. 135-143° at 14 mm.; n_D^{25} 1.5480-1.5500. Literature value:¹⁹ b.p. 137-139° at 12-13 mm. Second, 68.5 g. (0.50 moles) of the resulting hydrazine was added to 300 ml. (238 g., 4.1 moles) of acetone and refluxed for two hours. After standing overnight the acetone-water mixture was evaporated and the remaining solution vacuum distilled yielding 74.7 g. (84% yield) of colorless liquid: b.p. 119-125° at 7 mm.; n_D^{25} 1.5275-1.5283.

Anal. Calcd. for $C_{11}H_{16}N_2$: N, 15.90%. Found: N, 16.01%.

V. Preparation of acetone methylhydrazone.--This compound was prepared by drop-wise addition of 35.5 g. (0.77 moles) of methylhydrazine to 71.5 g. (1.21 moles) of acetone containing two drops of acetic acid as a catalyst. After an hour the reaction mixture was dried over potassium hydroxide pellets. Distillation of the reaction mixture followed by a second distillation of fractions boiling above 112° gave five portions totaling 40.0 g. (60% yield) of a colorless liquid with a stinging odor: b.p. 115-119° at 748 mm., n_D^{25} 1.4467-1.4476; λ_{max} 227 mμ., $\log \epsilon = 3.33$.

Anal. Calcd. for $C_4H_{10}N_2$: N, 32.52%. Found: N, 34.31%.

PREPARATION OF AZOACETATES.

I. Preparation of 2-acetoxy-2-phenylazopropane.--This azoacetate was prepared¹³ by slow addition of 29.6 g. (0.20 moles) of a solution of acetone phenylhydrazone dissolved in

75 ml. of methylene chloride to a solution of 98 g. (0.22 moles) of lead tetraacetate dissolved in 300 ml. of methylene chloride maintained at 6-10°. After stirring for 1.5 hours 150 ml. of saturated sodium bicarbonate solution and 50 ml. of water were added. The insoluble matter was separated by filtration through celite and the solution was washed with two more 50 ml. portions of the sodium bicarbonate solution and two 50 ml. portions of water. After drying with anhydrous sodium sulfate, the methylene chloride was vacuum evaporated and the residue vacuum distilled to give 32.3 g. (79% yield) of an orange oil: b.p. 136-139° at 14 mm.; n_D^{25} 1.5150-1.5165. Literature values:¹³ b.p. 89° at 1 mm.; n_D^{25} 1.5152.

II. Preparation of 1-acetoxy-1-phenylazocyclopentane.--This compound was prepared by adding a solution of 20.0 g. (0.115 moles) of cyclopentanone phenylhydrazone dissolved in 50 ml. of methylene chloride to a solution of 66 g. (0.15 moles) of lead tetraacetate dissolved in 200 ml. of methylene chloride while stirring and maintaining at 5-10°. Throughout the isolation of the product the atmosphere in each container was replaced with methane. After stirring an additional hour at room temperature the solution was washed with 100 ml. of water followed by 100 ml. of sodium bicarbonate. The solution was then filtered through celite and washed with three 50 ml. portions of water. After drying with anhydrous sodium sulfate the solvent was evaporated and after two

vacuum distillations four portions totaling 18.6 g. (70% yield) of an orange oil were obtained: b.p. 113-114° at 1 mm.; n_D^{25} 1.5358-1.5370; λ_{\max} 401 m μ ., $\log \epsilon = 2.29$; λ_{\max} 268 m μ ., $\log \epsilon = 4.04$.

Anal. Calc. for $C_{13}H_{16}N_2O_2$: C, 67.22%; H, 6.94%; N, 12.06%. Found: C, 67.19%; H, 7.01%; N, 12.07%.

III. Preparation of 1-acetoxy-1-phenylazocyclohexane.--A solution of 84.0 g. (0.45 moles) of freshly prepared cyclohexanone phenylhydrazone dissolved in 250 ml. of methylene chloride was added over a period of 45 minutes to a cold (5-10°) stirred solution of 220 g. (0.47 moles) of lead tetraacetate in 500 ml. of methylene chloride. After stirring another hour the methylene chloride solution was washed with 500 ml. of water, three 100 ml. portions of sodium bicarbonate and two 100 ml. portions of water. After drying with anhydrous sodium sulfate the methylene chloride was evaporated, the oil was dissolved in pentane, the insoluble matter was separated by filtration, the pentane was removed by evaporation and the oil was vacuum distilled to yield 49.3 g. (45% yield) of product: b.p. 141-144° at 1 mm.; n_D^{25} 1.5400-1.5415. Literature values:¹³ b.p. 137° at 1 mm.; n_D^{25} 1.5361.

IV. Preparation of 2-acetoxy-2- β -phenylethylazopropane.--A solution containing 35.2 g. (0.20 moles) of acetone β -phenylethylhydrazone in 100 ml. of methylene chloride was added to a 10° solution of 95.0 g. (0.22 moles) of lead tetraacetate while stirring. After stirring for another 45 minutes 200

ml. of water was added and the layers separated. The organic layer was then washed with a 100 ml. portion of water and two 100 ml. portions of saturated sodium bicarbonate followed by two 50 ml. portions of water. After drying with anhydrous sodium sulfate concentration by vacuum evaporation and vacuum distillation gave 14.1 g. (30% yield) of the azoacetate: b.p. 118-124° at 2 mm.; n_D^{25} 1.4947-1.4951. Literature values:¹³ b.p. 147° at 8 mm.; n_D^{23} 1.4967.

V. Preparation of 2-acetoxy-2-methylazopropane.--In this preparation 21.4 g. (0.25 moles) of acetone methylhydrazone dissolved in 40 ml. of methylene chloride was slowly added to a solution of 123.0 g. (0.25 moles) of lead tetraacetate in 250 ml. of methylene chloride which was maintained at 5-10°. After stirring another hour 250 ml. of water and 200 ml. saturated sodium bicarbonate solution were added and the brown solid which formed was removed by filtration through celite. The methylene chloride solution was then washed with another 100 ml. portion of sodium bicarbonate solution followed by 100 ml. of water and dried with anhydrous sodium sulfate. After concentration, vacuum distillation of the material gave 26.3 g. (73% yield) of a straw colored liquid: b.p. 82-89° at 101 mm.; n_D^{25} 1.4139-1.4150; λ_{max} 354 m μ ., $\log \epsilon = 2.59$. This compound became cloudy and developed a white solid within a week when left at room temperature.

Anal. Calcd. for $C_6H_{12}N_2O_2$: C, 49.99%; H, 8.39%; N, 19.43%. Found: C, 49.95%; H, 8.25%; N, 19.61%.

REACTION OF LITHIUM ALUMINUM HYDRIDE WITH AZOACETATES.

I. Preparation of 2-phenylazopropane.--Two experiments using different molar ratios of reactants have been performed. First, a solution of 14.4 g. (0.075 moles) of 2-acetoxy-2-phenylazopropane dissolved in 75 ml. of anhydrous ether was added drop-wise to a solution of 0.75 g. (0.019 moles) of lithium aluminum hydride partially dissolved in 100 ml. of anhydrous ether. The reaction was stirred and maintained at $0-10^{\circ}$ during the addition and for an hour thereafter. Then 50 ml. of water was added to destroy any excess hydride and to dissolve the acetates formed. The aqueous layer was separated and extracted with ether and the combined ether layers were dried with anhydrous sodium sulfate. Upon evaporation of the solvent and standing for two days the product evolved gas and became dark red. Vapor phase chromatography of this product at 130° gave a yellow liquid of which the infrared spectrum showed bands at 3320 and 1735 cm^{-1} . These bands are characteristic of N-H of acetone phenylhydrazone and C=O of the starting azoacetate.

Second, a solution of 10.3 g. (0.050 moles) of 2-acetoxy-2-phenylazopropane dissolved in 50 ml. of anhydrous ether was added over a period of one hour to a stirred solution of 3.0 g. (0.075 moles) of lithium aluminum hydride partially dissolved in 100 ml. of anhydrous ether and maintained at $0-10^{\circ}$. After stirring an additional hour at room temperature, refluxing for several hours, and standing overnight, the

excess lithium aluminum hydride was decomposed by adding 50 ml. of water and keeping the solution cool. The aqueous layer was separated and extracted and the combined ether layers dried over anhydrous sodium sulfate. After removing the ether by distillation at 34° , vapor phase chromatography at 42° showed one component which did not have the same retention time as known samples of benzene and isopropyl alcohol. This component was not further investigated. The high boiling products were observed by chromatography at 125° . Only one component was observed. The high boiling material was twice distilled and the second time three portions of 2-phenylazopropane totaling 1.3 g. (18% yield) were collected: b.p. $97-100^{\circ}$ at 17 mm.; n_D^{25} 1.5211; λ_{\max} 403 m μ ., $\log \epsilon = 3.94$. Literature values:¹⁰ b.p. 110° at 28 mm., n_D^{20} 1.5249. Three portions of yellow liquid totaling 3.4 g. and having b.p. $100-135^{\circ}$ at 17 mm. and n_D^{25} 1.5301-1.5467 were also obtained. The infrared spectrum of this oil showed a band at 3310 cm^{-1} which is characteristic of N-H of acetone phenylhydrazone. The entire spectrum, however, did not match that of authentic acetone phenylhydrazone indicating the material to be impure.

II. Reaction of 1-acetoxy-1-phenylazocyclopentane.--A solution of 7.5 g. (0.032 moles) of azoacetate dissolved in 80 ml. of anhydrous ether was added slowly to a cold ($0-10^{\circ}$) stirred solution of 1.9 g. (0.049 moles) of lithium aluminum hydride partially dissolved in 80 ml. of anhydrous ether.

After the addition the solution was refluxed for three hours and let stand overnight after which water was added to decompose the excess hydride. The ether layer was separated and dried with anhydrous sodium sulfate and the ether distilled until the temperature reached 37° . One gram (67% yield) of ethyl alcohol was collected: b.p. $76-77^{\circ}$; n_D^{25} 1.3621.

When this was mixed with an equal volume of known ethyl alcohol vapor phase chromatography at 70° showed only one component. Six portions of unidentified yellow oil totaling 3.9 g. were also collected: b.p. $96-130^{\circ}$ at 1 mm.; n_D^{25} 1.5528-1.5808. Of these the first four portions totaled 1.4 g. and had the following indices of refraction: n_D^{25} 1.5528, 1.5537, 1.5547 and 1.5560. A sample from the first portion was collected by vapor phase chromatography at 100° and had the following properties: n_D^{25} 1.5520; infrared absorption 3030, 2930, 2840, 1605, 1520, 1505, 1480, 1455, 1333, 1303, 1190, 1145, 1063, 1015, 915, 750 and 647 cm^{-1} . The fifth portion contained 1.8 g. (n_D^{25} 1.5661) and the sixth portion contained 0.7 g. (n_D^{25} 1.5808). Upon standing all portions darkened considerably and a white solid crystallized. After washing with pentane this solid decomposed at $82-86^{\circ}$. This system was not further investigated.

III. Reaction of 1-acetoxy-1-phenylazocyclohexane.--A solution of 12.3 g. (0.050 moles) of the azoacetate was added to 3.0 g. (0.075 moles) of lithium aluminum hydride in an ethereal solution. The reaction was then performed and

worked up in the above manner. There was no evidence for low boiling products. Vacuum distillation gave 6.5 g. of yellow oil which partially solidified: b.p. 112-136° at 1 mm.; n_D^{25} 1.5527-1.5687. Recrystallization of the solid from ethyl alcohol gave 0.8 g. (9% yield) of a pale yellow solid whose infrared spectrum was identical to the previously prepared cyclohexanone phenylhydrazone: m.p. 72-74°. Literature value:¹⁵ m.p. 74-76°.

A second reaction was performed by adding a solution of lithium aluminum hydride which was standardized by a modified method of Krynitsky, Johnson and Carhart.¹⁴ This involved injection of a known volume of lithium aluminum hydride solution by hyperdermic syringe into a 1.000 l. flask which contained dilute sulfuric acid and ether maintained at 0°. The pressure change due to evolution of hydrogen was determined and the ideal gas law was used to calculate the molarity. In the reaction which followed 60 ml. of 0.58 M lithium aluminum hydride (0.035 moles) were added to a cold ethereal solution of 12.3 g. (0.050 moles) of azoacetate. The reaction was then performed in the above manner giving evidence for four products. Vapor phase chromatography of the ether solution at 70° indicated components which had the same retention time as known samples of benzene and ethanol. Two portions of cyclohexanone totaling 0.83 g. (18% yield) were collected: b.p. 27° at 2 mm.; n_D^{25} 1.4496-1.4518; major infrared absorption at 1710 cm^{-1} . Bellamy⁵ reports cyclo-

hexanone to have C=O absorption from 1706-1720 cm^{-1} . Vapor phase chromatography of a mixture of this compound and known cyclohexanone at 70° gave only one peak. A total of 4.1 g. of yellow oil which partially solidified was also collected: b.p. 102-140° at 1 mm.; n_D^{25} 1.5640-1.5844. The portions containing solid were dissolved in ethanol and water and recrystallized giving 1.8 g. (19% yield) of pale orange needles of cyclohexanone phenylhydrazone: m.p. 74-76°. Literature value:¹⁵ m.p. 74-76°. The infrared spectrum of this oil showed also a trace of the starting azoacetate. It showed a weak band at 1733 cm^{-1} . The azoacetate has a major absorption band at 1733 cm^{-1} .

IV. Preparation of 2- β -phenylethylazopropane.--An ether solution of 7.07 g. (0.030 moles) of 2-acetoxy-2- β -phenylethylazopropane was added to a cold ether solution of 1.8 g. (0.045 moles) of lithium aluminum hydride over a period of 10 minutes. After stirring for one hour at about 10° the mixture was refluxed for 2 hours and let stand for 6 hours. The excess lithium aluminum hydride was decomposed with water. After washing and separating the organic layer was dried with anhydrous sodium sulfate and the ether distilled at 34°. The remaining solution was investigated with vapor phase chromatography programmed from 70-230° at 20° per minute. One component had the same retention time as ethylbenzene. The azo and hydrazone compounds were also present. A reference mixture of 0.0247 g. (1.40×10^{-4} moles) of

2- β -phenylethylazopropane, 0.0247 g. (1.40×10^{-4} moles) of acetone β -phenylethylhydrazone, and 0.0193 g. (1.44×10^{-4} moles) of t-butylbenzene, an internal standard, was prepared. The ratios of the peak areas for these compounds were 1.13 : 0.550 : 1.00 respectively. The internal standard, 0.511 g. of t-butylbenzene, was added to 4.00 ml. of the reaction product. Vapor phase chromatography then gave the following ratios of areas for the azo compound, hydrazone, and standard: 0.770 : 0.874 : 1.00. For a total volume of 9.75 ml. this represents 2.60 g. (49% yield) of acetone β -phenylethylhydrazone and 1.13 g. (21% yield) of 2- β -phenylethylazopropane. The hydrazone was identified by comparison of the infrared spectra of a sample collected from vapor phase chromatography to the previously prepared hydrazone. The new azo compound had the following properties: n_D^{25} 1.4920; λ_{\max} 355 m μ ., $\log \epsilon = 2.17$.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95%; H, 9.15%; N, 15.90%. Found: C, 74.80%; H, 8.92%; N, 16.06%.

V. Reaction of 2-acetoxy-2-methylazopropane.--A solution of 12.0 g. (0.084 moles) of this azoacetate was added slowly to a cold solution of 5.0 g. (0.13 moles) of lithium aluminum hydride. After stirring for 1.5 hours at 10° the mixture was stirred about 5 hours at room temperature. Water was then added to decompose the excess hydride and the ether layer was washed with water and dried with anhydrous sodium sulfate. After distilling the ether at 34° the remaining

solution was analyzed with vapor phase chromatography programmed from 60-100° at 10° per minute and 100-230° at 30° per minute. Three components were found. These did not have the same retention time as the starting azoacetate or the related hydrazone. Samples were collected and all three were colorless. Even though infrared spectra were obtained, no conclusion regarding the identity of the substances was reached.

A second reaction was performed as above except after the addition the solution was stirred for only one hour before decomposing the excess lithium aluminum hydride. Vapor phase chromatography showed traces of the starting azoacetate as well as the three previously encountered components.

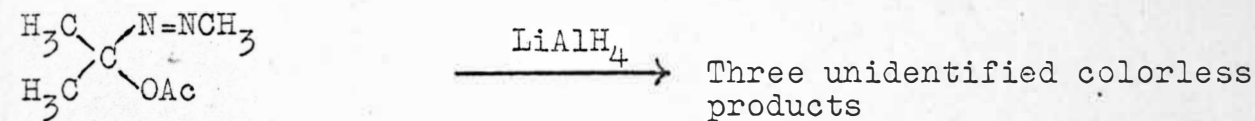
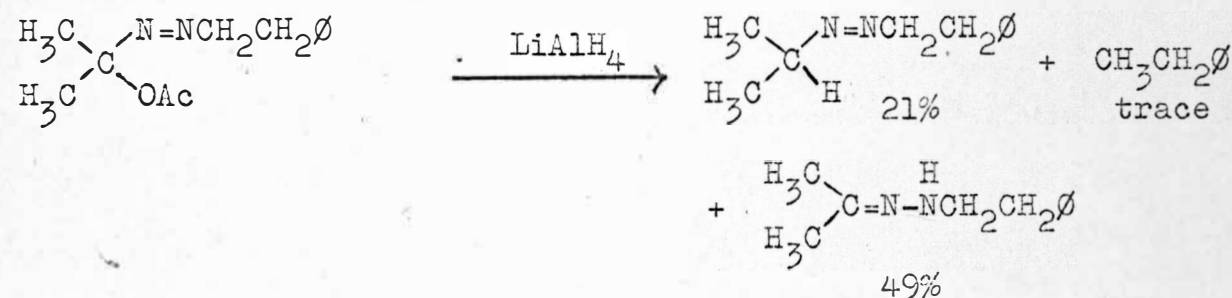
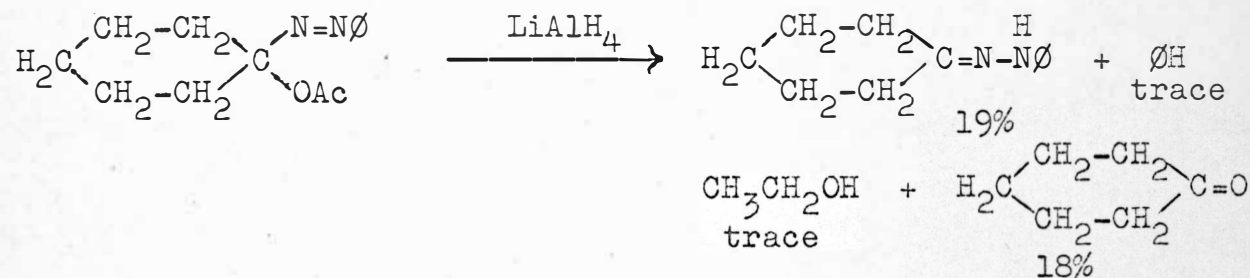
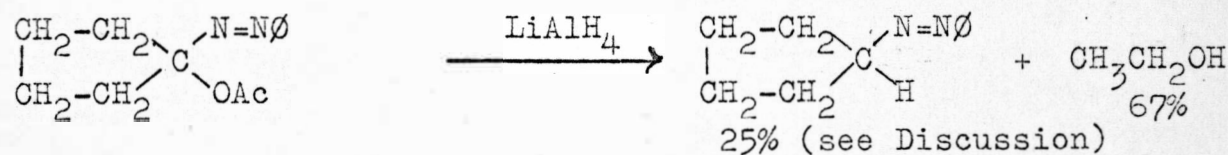
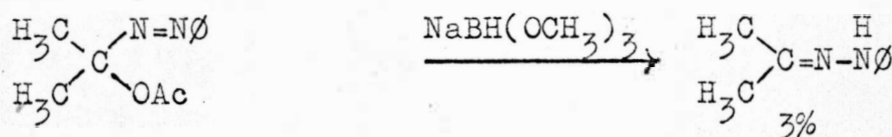
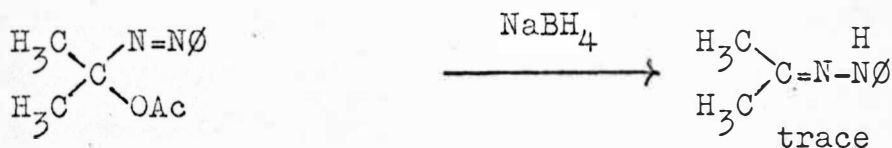
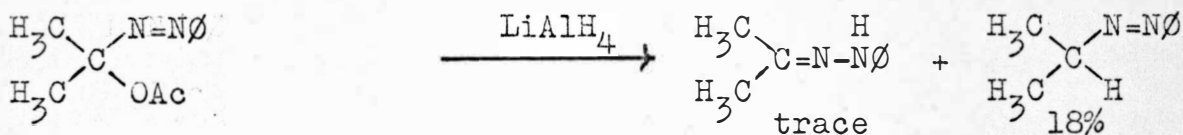
REACTION OF 2-ACETOXY-2-PHENYLAZOPROPANE WITH OTHER HYDRIDES.

I. Reaction with sodium borohydride.--A 10.3 g. (0.050 moles) portion of the azoacetate was added to a solution of 3.8 g. (0.10 moles) of sodium borohydride in 75% aqueous methanol at room temperature. After 10 hours the white insoluble matter was separated by filtration, 100 ml. of water was added, and the solution was extracted with pentane. The orange pentane solution was dried with anhydrous sodium sulfate and the pentane distilled at 36°. The remaining solution was vacuum distilled giving 10 portions totaling 1.9 g. of oil: b.p. 97-128° at 2 mm.; n_D^{25} 1.5519-1.6140.

Infrared spectra of the first, fifth, and tenth portions all showed bands near 3320 and 1735 cm^{-1} giving evidence for acetone phenylhydrazone and the starting azoacetate respectively.

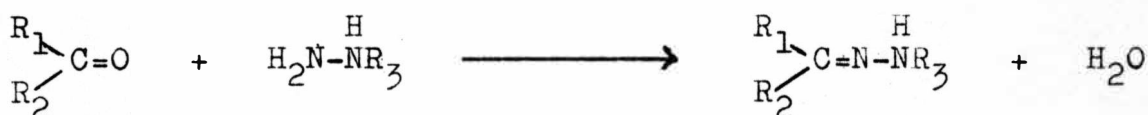
II. Reaction with sodium trimethoxyborohydride.--Six and a half grams (0.032 moles) of the azoacetate dissolved in 30 ml. of dioxane was added to 4.5 g. (0.035 moles) of sodium trimethoxyborohydride partially dissolved in 150 ml. of water. After refluxing overnight the solution was diluted with water, extracted with pentane, dried with anhydrous sodium sulfate and concentrated. The remaining red oil was vacuum distilled giving five portions of oil totaling 0.7 g.: b.p. 83-140° at 4 mm.; n_D^{25} 1.5260-1.5838. The infrared spectrum of the first portion showed bands at 3320 and 1735 cm^{-1} giving evidence for both the hydrazone and the azoacetate. The infrared spectrum of the fourth portion did not have a band at 1735 cm^{-1} . Furthermore, the rest of the spectrum of portion four matched that of known acetone phenylhydrazone. The fourth and the fifth portions which had n_D^{25} 1.5811 and 1.5838 respectively totaled 0.14 g. (3% yield) of acetone phenylhydrazone.

SUMMARY OF ATTEMPTED REACTIONS OF HYDRIDES WITH AZOACETATES

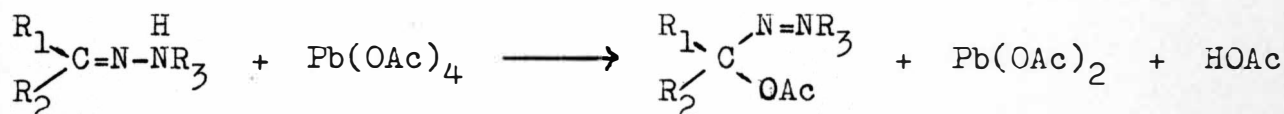


DISCUSSION

This research can be divided into three parts, the preparation of hydrazones, the preparation of azoacetates, and the reaction of hydrides with azoacetates. The last of these represents the main portion of the research. The preparation of hydrazones involved the condensation of a ketone and a substituted hydrazine to give the ketohydrazone:

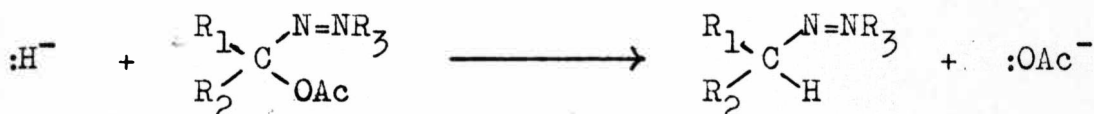


The preparation of azoacetates by oxidation of the ketohydrazone with lead tetraacetate is also a standard procedure:¹³



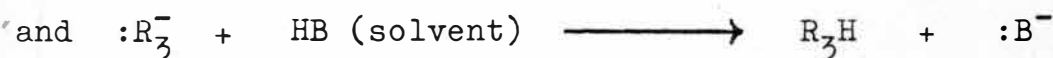
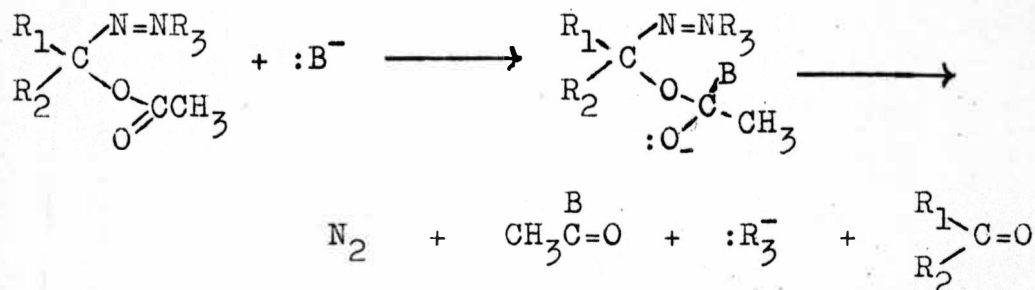
Among the azoacetates prepared two, 2-acetoxy-2-methylazopropane and 1-acetoxy-1-phenylazocyclopentane, have not been previously reported.

The reaction of hydrides with azoacetates in ether was believed to involve an $\text{S}_{\text{N}}2$ mechanism with the acetate displaced by the nucleophilic hydride yielding an unsubstituted aliphatic or aliphatic-aromatic azo compound:

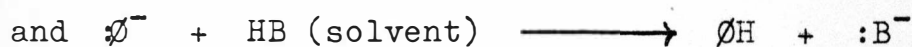
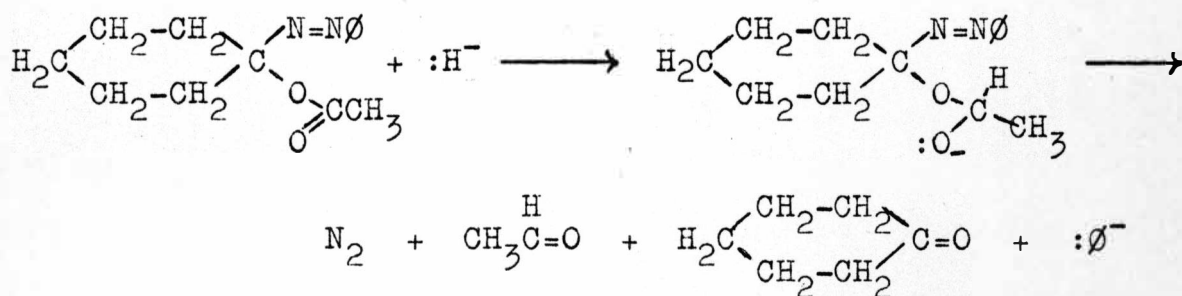


However, observation of the various products obtained showed the reaction was not this simple. In the several reactions

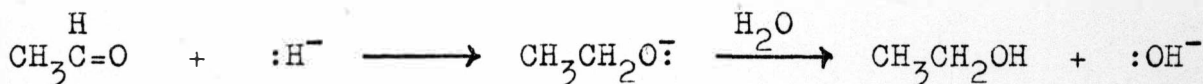
examined the formation of benzene, ethylbenzene and ketones is consistent with the mechanism of base decomposition of azoacetates:¹²



The above decomposition will explain the formation of benzene and cyclohexanone in the reaction of 1-acetoxy-1-phenylazocyclohexane:



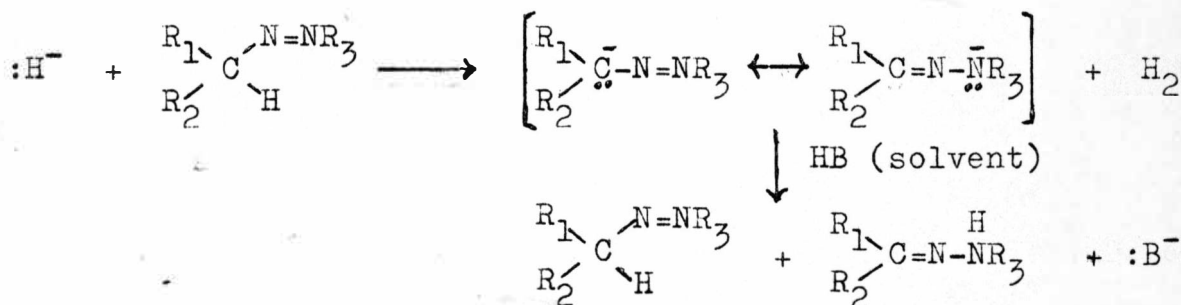
The ethyl alcohol which was also observed may be formed by reduction of acetaldehyde:



The formation of ethyl alcohol may result from hydride reduction of the acetate ion produced in the S_N2 displacement and, therefore, is not diagnostic of the reaction occurring. Also, base decomposition explains the ethyl-

benzene formed in the reaction of 2-acetoxy-2- β -phenyl-ethylazopropane. The lack of base decomposition products in the other reactions is not astonishing since ethyl alcohol, acetone or its reduction product, 2-propanol, in the 2-propane series could have been lost in the water wash after the initial reaction.

A further complication is the formation of the related hydrazone. In all except the reaction of 2-acetoxy-2-phenylazopropane with lithium aluminum hydride the amounts of azo compounds identified were less than the related hydrazones. Bellamy and Guthrie³ have shown that tautomerism of the azo and hydrazone forms in neutral solution as reported by O'Connor¹⁵ is incorrect. However, in basic solution Bellamy and Guthrie⁴ found tautomerism does exist. Among the azo compounds subjected to treatment with sodium methoxide in methanol they found 2-phenylazopropane yielded 47% acetone phenylhydrazone and phenylazocyclohexane yielded 45% cyclohexanone phenylhydrazone. Since hydride ion is a stronger base than methoxide tautomerism is very plausible although ether is not as polar as methanol:



Separation of the azo and hydrazone compounds was also

a problem. In all reactions attempts were made to identify and determine the amounts of these products by vapor phase chromatography. However, only with the reactions of 2-acetoxy-2-phenylazopropane and 2-acetoxy-2- β -phenylethylazopropane have consistent results been obtained. In the other systems experimental conditions were not discovered which would adequately resolve these pairs of compounds. Decomposition on the chromatographic column also occurred.

Since the boiling points of the azo and hydrazone compounds are not widely separated vacuum distillation gives a mixture of these products. This is evident in the distillation of 2-phenylazopropane which had the following properties: b.p. 97-100° at 17 mm. and n_D^{25} 1.5211. These properties for acetone phenylhydrazone are: b.p. 140° at 16 mm.⁶ and n_D^{26} 1.585³. The susceptibility of these compounds to thermal decomposition precluded the use of a fractionation column which may have improved the efficiency of separation. Further consideration of the additional 3.4 g. of yellow oil (b.p. 100-135° at 17 mm., n_D^{25} 1.5301-1.5467 and infrared N-H absorption at 3310 cm⁻¹) obtained in the reduction of 2-acetoxy-2-phenylazopropane leads to the conclusion that this is a mixture of 2-phenylazopropane and acetone phenylhydrazone. Considered this way, the sum of the yields of these two compounds is 64%.

A similar situation exists with the reaction of 1-acetoxy-1-phenylazocyclohexane. Six and a half grams of yellow oil

were obtained: b.p. 112-136° at 1 mm., n_D^{25} 1.5527-1.5687 (portions which did not completely solidify). The higher boiling portions solidified and were identified as cyclohexanone phenylhydrazone. The known literature values of phenylazocyclohexane are: b.p. 106-112° at 3 mm., $n_D^{26.5}$ 1.5503.¹⁵ Again this suggests the presence of the azo and hydrazone forms. Cyclohexanone phenylhydrazone and phenylazocyclohexane would give a combined yield of 68%. In the reverse addition, addition of hydride to azoacetate, the above conclusions are not valid since traces of the starting azoacetate and cyclohexanone were present in the high boiling material.

Comparison of the properties of the first four portions of the product from the reaction of 1-acetoxy-1-phenylazocyclopentane with those of phenylazocyclohexane indicates that this could be phenylazocyclopentane. Properties of phenylazocyclopentane are not reported. However, since the structure and bonding of these two azo compounds are similar their properties should also be similar. The first portion of the product had the following properties: b.p. 96° at 1 mm., n_D^{25} 1.5528. Also, the infrared spectrum of a sample collected from vapor phase chromatography with n_D^{25} 1.5520 gave no evidence for N-H or C=O. Considered this way the 1.4 g. of oil obtained represents a 25% yield of phenylazocyclopentane.

The presence of ethyl alcohol could indicate reduction

of the acetate ester since reduction of esters is a common reaction with lithium aluminum hydride. Therefore, less powerful reducing agents such as sodium borohydride and sodium trimethoxyborohydride which do not reduce esters were also employed. However, these reactions were less successful than those with lithium aluminum hydride since only very small amounts of high boiling material which contained traces of the starting azoacetate were obtained.

In regard to the stoichiometry a molar ratio of 2:3 of azoacetate to lithium aluminum hydride was found to be best. Starting azoacetate was detected in the systems with the following molar ratios and reaction times: 2-acetoxy-2-phenylazopropane, 4:1, 1 hour; 1-acetoxy-1-phenylazocyclohexane, 3:2, 3 hours; 2-acetoxy-2-methylazopropane, 2:3, 1 hour. However, a ratio of 2:3 in the 2-acetoxy-2-phenylazopropane series gave no starting material when reacted for 2 hours. In the remaining systems a ratio of 2:3 was used with reaction times of 2-9 hours with no trace of the starting azoacetate.

SUMMARY

Five reactions of azoacetates with lithium-aluminum hydride have been studied. This study resulted in the preparation of two unreported azoacetates, 1-acetoxy-1-phenylazocyclopentane and 2-acetoxy-2-methylazopropane, and one new azo compound, 2- β -phenylethylazopropane. However, this reaction is not a practicable method of synthesis of azo compounds. The yield of azo compounds is low. This is believed to be a result of the competing base decomposition of azoacetates and the base catalyzed tautomerism of azo and hydrazone compounds. The azo compounds in the reaction mixtures thus obtained are difficult to purify by distillation.

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VITA

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