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## A Study of the Base Catalyzed Decompositions of Azoacetates

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A STUDY OF THE BASE CATALYZED  
DECOMPOSITIONS OF AZOACETATES

by

David V. Herman

A Thesis submitted to the  
Faculty of the School of Graduate  
Studies in partial fulfillment  
of the  
Degree of Master of Arts

Western Michigan University  
Kalamazoo, Michigan  
July 1966

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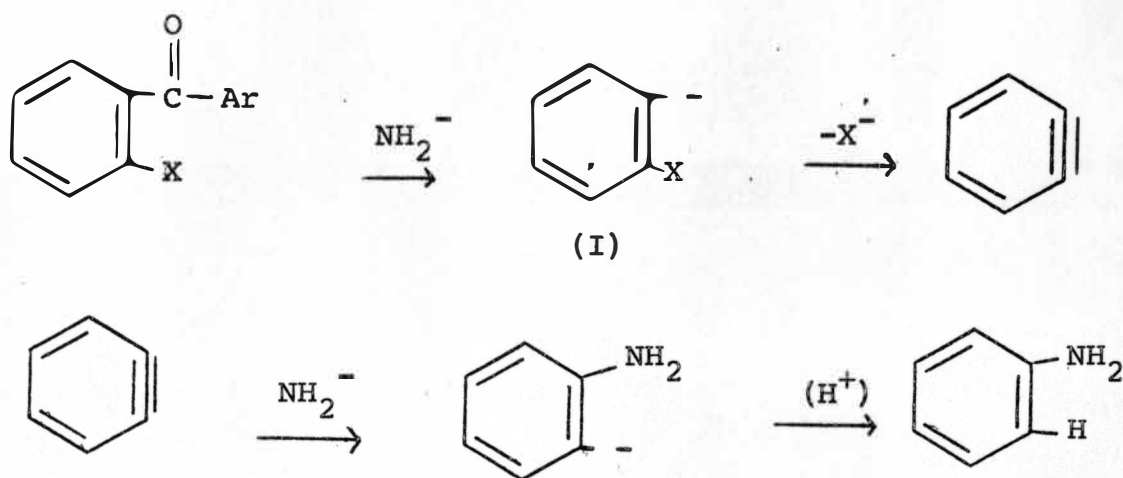
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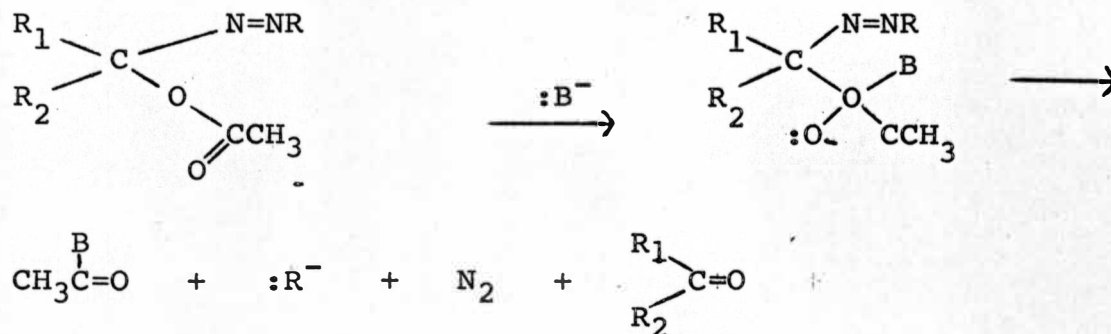
## INTRODUCTION

The formation of a benzyne intermediate has been (2,5,6) shown by several investigators to be developed in at least four different reactions; the reaction of o-dihalobenzenes with magnesium or lithium, aryl halides with strong nucleophiles, o-halobenzophenones with potassium amide in liquid ammonia, and the decomposition (13) of benzenediazonium-2-carboxylate. The mechanism proposed for one of the above most relevant to the following study, the reaction of o-halobenzophenones with potassium amide in liquid ammonia, is outlined in the following sequence:



It has been demonstrated recently that in protonic solvents, the base catalyzed decomposition of an azoacetate

gives a hydrocarbon, nitrogen, a ketone and an acetate  
(9)  
salt. The mechanism which is believed to be involved  
in this decomposition is the following:



Since this process involves the development of a carbanion intermediate, the presence of a suitable leaving group on an aryl carbanion formed in this manner may lead to a new route to benzyne. Thus it was thought that if R were an o-halophenyl and the reaction media were non-protonic the carbanion would be diverted to produce an intermediate identical to (I) in the o-halobenzophenones-potassium amide reaction.

In the event that the postulated process actually forms a benzyne, the benzyne may be detected in the conventional manner by adding a trapping agent, isolating and identifying the reaction products.

This proposed new route to the benzyne appears to

have the following advantages: simple reaction conditions and simply prepared precursor. Typical azoacetates related to the compounds needed in this study have been prepared recently in good yields by the oxidation of the hydrazones (10) with lead tetraacetate.

## LITERATURE SURVEY

The characteristics of the benzyne type of intermediate (2,5,6) is described in several recent review articles. One of the types of experimental observation that gives strongest support to the existence of a benzyne intermediate is the formation of common reaction products from certain isomeric reactants. Thus 1- and 2-chloro, or 1- and 2-iodonaphthalenes react with lithium piperidide in ether to give the same ratio of N-naphthylpiperidines. (6) Identical ratios of products show that a common intermediate is present.

(4)  
It was shown by Roberts that chlorobenzene-1-C<sup>14</sup> and potassium amide in liquid ammonia gives nearly equal molar quantities of aniline-1-C<sup>14</sup> and aniline-2-C<sup>14</sup>. Iodobenzene-1-C<sup>14</sup> gave a similar mixture. These and other experimental results are currently best explained by a benzyne intermediate.

The reactions which result in the formation of benzyne intermediates are of four general types:  
o-halobenzophenones with potassium amide in liquid ammonia, arylhalides with strong nucleophiles (i.e.,



lithium piperidide), o-dihalobenzene with magnesium or lithium and the decomposition of benzenediazonium-2-carboxylates in non-basic media. The first three methods require very strong bases, while the fourth generates benzyne by the pyrolysis of benzenediazonium-2-carboxylates at  $35^{\circ}$ - $60^{\circ}$ , in which nitrogen and carbon dioxide are formed. This reaction is noteworthy in that a strong electrophilic reagent, benzyne, is developed in a weakly acidic media.

The standard methods of identification of benzyne intermediates are: the formation of addition products via the Diels-Alder addition or evidence that both positions in the aryl ring become almost identical.

A benzyne is electrophilic and adds to a diene. The product of such a reaction may be isolated when reactions producing benzyne intermediates are carried out in the presence of a diene. The addition of benzyne to dienes such as anthracene and furan have been used by Stiles (13) to show that benzyne was formed during the decomposition of benzenediazonium-2-carboxylates.

The second method requires that the ring be labeled so that the ring positions may be differentiated. This may be accomplished by isotopic labeling or by ring

substitution. If product composition indicates that the positions become nearly identical, the mechanism is elimination-addition, via benzyne formation, rather than the substitution-elimination sequence.

For the purposes of this study it was decided to apply the trapping method to detect benzyne intermediates if generated.

The necessary o-halophenylhydrazines may be prepared from o-haloanilines via the reduction of the diazonium salts. The diazonium salts are preparable by the standard methods via diazotization with sodium nitrite in excess concentrated hydrochloric acid. Diazonium salts are most satisfactorily reduced using stannous chloride and (1) hydrochloric acid.

The o-halophenylhydrazines may be converted to the acetone o-halophenylhydrazones by the common condensation with excess acetone. The azoacetates may be prepared by the lead tetraacetate oxidation of the acetone o-halophenylhydrazones.

## EXPERIMENTAL

In the experimental section all boiling points are uncorrected and in degrees centigrade. Vapor phase chromatography was performed with an F and M Model 720 dual column programmed temperature gas chromatograph with a Disc integrator. The infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer. The ultraviolet spectra were measured with a Beckman Model DB recording spectrophotometer using 95% ethanol as a solvent. The proton resonance spectra were recorded with a Varian A-60 spectrometer. Galbraith Microanalytical Laboratories, Knoxville, Tennessee performed the elemental analyses.

### PREPARATION OF o-HALOPHENYLHYDRAZINES

o-Fluoro, o-chloro and o-iodophenylhydrazines were prepared by the stannous chloride reduction of o-halobenzenediazonium salts according to the method of (14) Suschitzky and isolated as the hydrochloride salts. These compounds gave the properties summarized in Table I.

Table I

Yields and Properties of  
o-Halophenylhydrazine Hydrochlorides

| o-Halogen | Yield | M.p.                 |
|-----------|-------|----------------------|
| F         | 46.1% | 185-187 <sup>a</sup> |
| Cl        | 50.7  | 195 <sup>b</sup>     |
| I         | 62.4  | 168 <sup>c</sup>     |

(14) (1)

a) Lit. value: 186<sup>o</sup>. b) Lit. value: 198-200<sup>o</sup>.  
 c) Lit. value: (7) 157-159<sup>o</sup>.

The o-fluoro and o-chloroanilines were commercially available. o-Nitroaniline was converted to o-iodonitro-  
 (12)  
 benzene via the diazonium salt. Reduction of the  
 o-iodonitrobenzene using hydrazine hydrate according to  
 (11)  
 Leggetter provided the o-iodoaniline, m.p. 56-58<sup>o</sup>;  
 (11)  
 Literature value: m.p. 60-61<sup>o</sup>.

#### PREPARATION OF ACETONE o-HALOPHENYLHYDRAZONES

The hydrazones were prepared by the conventional condensation of hydrazine with a ketone. A typical preparation of a hydrazone follows:

A mixture consisting of 36.1 g. (0.253 mole) of o-chlorophenyl hydrazine, 50 ml. (39.5 g., 0.68 mole) of

acetone and 1 ml. of glacial acetic acid was refluxed for two hours. After 150 ml. of water was added, the hydrazone was extracted with three 50 ml. portions of ether. The combined ether extracts were dried with anhydrous potassium carbonate and concentrated by vacuum evaporation. The oil remaining was vacuum distilled to yield 29.5 g. (68%) of acetone o-chlorophenylhydrazone having the properties indicated in Table II.

The o-iodo and o-fluorophenylhydrazones were prepared in an analogous manner with the exception that the hydrazine hydrochloride and an equivalent amount of sodium acetate was used as the source of the hydrazine.

The yields and properties of the hydrazones prepared are summarized in Table II.

Table II

Yields and Properties of  
Acetone o-Halophenylhydrazones

| o-Halogen | Yield | B.p.            | $n_D^{25}$          |
|-----------|-------|-----------------|---------------------|
| F         | 40%   | 108-114 @ 5 mm. | 1.5530              |
| Cl        | 64    | 103-104 @ 1 mm. | 1.5798 <sup>a</sup> |
| I         | 68    | 155-158 @ 1 mm. | 1.6310              |

a) Lit. value: <sup>(3)</sup> 1.5816 @ 21°

PREPARATION OF 2-(o-HALOPHENYLAZO)-2-PROPYL ACETATES  
(10)

The method of Iffland, Salisbury and Schafer was used to prepare the azoacetates. This method consists of oxidation of the hydrazone with lead tetraacetate. The procedure was the same for all azoacetates and the following preparation is representative.

A solution consisting of 4.06 g. (0.025 mole) of acetone o-fluorophenylhydrazone dissolved in 15 ml. of methylene chloride was added slowly to a cold (0°) solution of 12 g. (0.027 mole) of lead tetraacetate dissolved in 50 ml. of methylene chloride. After addition was completed, the mixture was added to 50 ml. of water and 100 ml. of saturated sodium bicarbonate solution. The insoluble material was removed by filtration through a Celite mat. The methylene chloride solution was separated, dried with anhydrous sodium sulfate and concentrated by vacuum evaporation. The residue was distilled to provide 4.5 g. (82%) of 2-(o-fluorophenylazo)-2-propyl acetate having the properties and analyses indicated in Table III.

The infrared and proton resonance spectra of these compounds were obtained and were consistent with the assigned structures and analogous to the spectra of

Table III

Properties and Analyses of  
2-(o-Halophenylazo)-2-Propyl Acetates

| o-Halogen | Yield | B.p.                | $\lambda_{\max}$ | $E_{\max}$ | $N_D^{25}$ | Analysis <sup>a</sup> |      |       |
|-----------|-------|---------------------|------------------|------------|------------|-----------------------|------|-------|
|           |       |                     |                  |            |            | C                     | H    | N     |
| F         | 82%   | 134-135<br>@ 10 mm. | 402 m $\mu$      | 466        | 1.5025     | 58.73                 | 5.72 | 12.59 |
|           |       |                     | 264              | 15,600     |            | 58.92                 | 5.84 | 12.50 |
|           |       |                     | 215              | 6,050      |            |                       |      |       |
| Cl        | 58    | 132-133<br>@ 3 mm.  | 406              | 204        | 1.5266     | 54.99                 | 5.40 | 11.85 |
|           |       |                     | 267              | 8,026      |            | 54.91                 | 5.44 | 11.64 |
| I         | 59    | 148<br>@ 1 mm.      | 268              | 532        | 1.5730     | 39.93                 | 4.04 | 8.30  |
|           |       |                     | 222              | 1,268      |            | 39.77                 | 3.94 | 8.44  |

a) The second value indicated is calculated from the appropriate molecular formula.

(10)

authentic 2-phenylazo-2-propyl acetate.

The preparation of potassium t-butoxide was carried out by slow addition of 20 g. (0.5 mole) of potassium to 100 ml. (1.0 mole) of t-butyl alcohol. The reaction mixture was heated to about 60° to complete the reaction. The excess t-butyl alcohol was removed by vacuum evaporation and the potassium t-butoxide dried at 100° under 1 mm. for 6 hours. A nmr spectra was obtained of a saturated solution of the potassium t-butoxide in dry benzene. A peak was observed at 1.07 ppm. downfield from TMS which corresponds to the aliphatic hydrogen atoms, however no peak was observed that would correspond to a hydroxyl proton. After the addition of a trace of t-butanol to the previous solution, an additional peak was observed at 1.75 ppm. and may be assigned to the hydroxyl hydrogen.

#### BASE CATALYZED DECOMPOSITIONS OF 2-(o-HALOPHENYLAZO)-2-PROPYL ACETATES

##### I. Decompositions of Azoacetates in Protonic Media.--

In order to develop a standardized procedure for the decomposition in protonic media the following reaction was conducted in which the nitrogen gas formed was



collected and used as a measure of the extent of the reaction. A 0.21 g. (0.001 mole) sample of 2-(o-chlorophenylazo)-2-propyl acetate was decomposed at 25° in 10 ml. of saturated potassium hydroxide methanol solution. After 6 hours reaction time the collected volume of nitrogen was 16 ml. and after 24 hours the volume was 20.0 ml. This corresponds to 75% of theory. A 100% yield of nitrogen collected over water at 25° and at 730 mm. pressure would have been 26.7 ml.

The series of azoacetates prepared were decomposed in protonic media and the halobenzenes formed were quantitatively determined by vapor phase chromatography. The decomposition of 2-(o-fluorophenylazo)-2-propyl acetate is typical. A 2.24 g. (0.01 mole) sample of the 2-(o-fluorophenylazo)-2-propyl acetate was added slowly to 25 ml. of a solution of 100 ml. of methanol, 20 g. of potassium hydroxide and 20 ml. of water. The decomposition was conducted in a 50 ml. Erlenmeyer flask fitted with a reflux condenser and a magnetic stirrer. After addition was complete the condenser was rinsed with 5 ml. of methanol. The decomposition mixture was stirred overnight. The mixture was added to 100 ml. of water and extracted twice with 20 ml. portions of p-xylene. The

p-xylene extracts were combined, dried with calcium chloride, then diluted to 50 ml. in a volumetric flask. A 10.00 ml. aliquot was mixed with 0.1675 g. of p-chlorotoluene. This mixture was washed twice with 20 ml. of water to remove traces of acetone and dried over calcium chloride. The mixture was analyzed by vapor phase chromatography and the amount of halobenzene was estimated using a working curve previously prepared from the examination of four mixtures containing known amounts of the halobenzene and the internal standard, in this case, p-chlorotoluene. The ratio of weights vs. the ratio of the peak areas were plotted. A 6 ft. x 1/4 in. column containing a packing prepared from diethylene glycol succinate (10% by weight) on firebrick was used at 110° and with a helium carrier gas flow of 30 cc. per minute. The peak areas were measured using a Disc integrator and averaged from four sample injections.

For the four mixtures of fluorobenzene and p-chlorotoluene having known composition the weight and the peak area ratios were respectively: 0.9808, 1.024; 0.9052, 0.920; 1.5224, 1.634; and 1.3344, 1.415. These values are shown in Fig. I. The aliquot of the reaction mixture gave an area ratio of 0.954 which corresponds to

0.779 g. (80%) of fluorobenzene in the decomposition.

Similar analytical procedures were completed for the chlorobenzene and iodobenzene using bromobenzene and p-chlorotoluene respectively as internal standards. Appropriate column temperatures were employed. These results are summarized in Table IV.

Table IV

Yields of Halobenzenes in  
Azoacetate Decompositions

| o-Halogen | Aqueous<br>Methanol | p-Xylene |
|-----------|---------------------|----------|
| F         | 80%                 | 80%      |
| Cl        | 70                  | *        |
| I         | 52                  | 36**     |

\*Volume of nitrogen measured as 75%

\*\*Triptycene detected in trace amounts.

II. Non-Protonic Media.--The following reaction was conducted in which the nitrogen gas formed was collected and used as a measure of the extent of the reaction. A 0.219 g. (0.001 mole) sample of 2-(o-chlorophenylazo)-2-propyl acetate was decomposed at 25° with a solution of 1 g. of potassium t-butoxide in 10 ml. of benzene dried over calcium hydride for two days. After 2 hours

the volume of nitrogen collected was 20.5 ml. and after 24 hours no additional nitrogen had been collected. This corresponds to 74.5% of theory. The theoretical volume of nitrogen measured over water at 25° and at 730 mm. pressure would have been 27.5 ml.

The 2-(o-halophenylazo)-2-propyl acetates were decomposed in a p-xylene solution containing potassium t-butoxide as base catalyst and anthracene as benzyne trapping agent. The p-xylene had been previously dried over calcium hydride. The halobenzenes produced were quantitatively measured by the analytical method developed for the decompositions in aqueous alcohol. The standardized method is illustrated for the decomposition of 2-(o-fluorophenylazo)-2-propyl acetate. A solution of 2.22 g. (9.86 mmoles) of 2-(o-fluorophenylazo)-2-propyl acetate dissolved in 25 ml. of dry p-xylene was added slowly to a stirred suspension of 2.7 g. (0.015 mole) of anthracene, 2.3 g. (0.02 mole) of potassium t-butoxide in 20 ml. of dry p-xylene. The reaction mixture was contained in a 50 ml. flask fitted with a condenser and magnetic stirrer. The addition required one hour and the mixture was stirred overnight. The reaction mixture was extracted with two 50 ml.

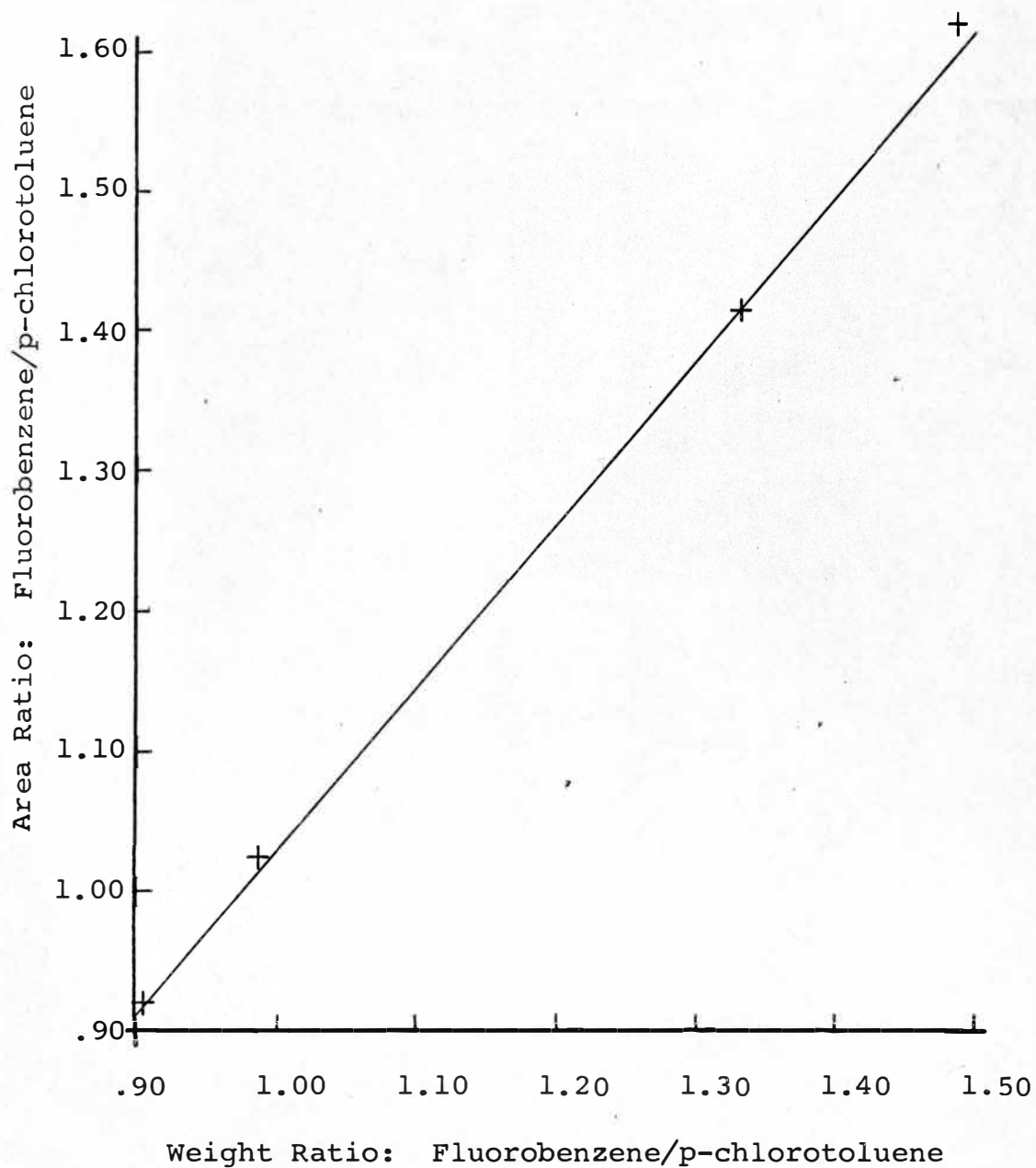
portions of water, dried over calcium chloride and examined by vapor phase chromatography for fluorobenzene. The yields of halobenzenes from these reactions are summarized in Table IV.

The reaction mixture from the decomposition of 2-(o-iodophenylazo)-2-propyl acetate was examined by vapor phase chromatography with the same column conditions (DEGS column stationary phase) as the analysis for iodobenzene except that the temperature was programmed at  $10^{\circ}$  per min. from  $130^{\circ}$  to  $240^{\circ}$ . Peaks for two components having retention times greater than the value for iodobenzene were observed. The retention time of one of these was identical to the retention time observed with authentic triptycene under the same operating conditions. This analysis for triptycene was repeated after changing the column and operating conditions to the following: 2 ft. x  $1/4$  in. column containing 15% by weight SE-30 on firebrick, column temperature, isothermal at  $220^{\circ}$ ; a helium flow of 60 cc. per min. Again a component peak appeared having the same retention time as that for authentic triptycene under these conditions. Several larger sample injections enabled collection of a

small sample of this component. Infrared spectra of this material showed all of the absorption bands observed in the spectra of authentic triptycene.

FIGURE I

Analytical Work Curve for  
Determination of Fluorobenzene



## DISCUSSION

This study can be divided into two parts: 1) the preparation of the azoacetates and 2) the decomposition of the azoacetates.

Following the preparation of the o-halophenylhydrazines by adapting published procedures, the hydrazones were formed by the condensation of the o-halophenylhydrazines with acetone. The synthesis of the azoacetates was accomplished by using the standard oxidation of a ketohydrazone with lead tetraacetate. The three azoacetates prepared, 2-(o-fluorophenylazo)-2-propyl acetate, 2-(o-chlorophenylazo)-2-propyl acetate, and 2-(o-iodophenylazo)-2-propyl acetate, have not been described previously. The assigned structures were supported by elemental analysis; infrared and proton resonance spectra.

The decompositions may be classified into two types: 1) reactions in protonic media and 2) reactions in non-protonic media. The azoacetates were first decomposed in an aqueous-methanolic solution as employed earlier in order to demonstrate the occurrence of the



base catalyzed decomposition process at room temperature and to measure the extent of this reaction through a measurement of the nitrogen and halobenzenes produced. The yields of the halobenzenes were determined by vapor phase chromatography. The same analytical procedure was used for both the aqueous and the non-aqueous reactions with a particular azoacetate. The relatively high yields of the halobenzenes in the aqueous decompositions of 2-(o-chlorophenylazo)-2-propyl acetate and 2-(o-fluorophenylazo)-2-propyl acetate were expected. This expectation was based on the high yield of benzene observed for the decomposition of 2-phenylazo-2-propyl acetate in aqueous-methanol. The lower yield of iodobenzene may be a consequence of incomplete decomposition. This lower yield of iodobenzene is not likely a result of the intervention of benzyne formation in view of the very low yield of benzyne related products formed in the latter experiments where benzyne formation was more favorable.

The decomposition reactions in non-protonic media were conducted in anhydrous p-xylene since its retention time was sufficiently different from the retention times

of the halobenzenes to permit analysis by vapor phase chromatography. Because of its significant solubility in aromatic hydrocarbons, potassium t-butoxide was used as the base catalyst. The reaction mixtures contained added anthracene to serve as benzyne trapping agent. As shown in Table IV, a relatively high yield of fluorobenzene was produced comparable to the yield observed in the decomposition in protonic media. The yield of iodobenzene was markedly less than that observed in the decomposition in protonic media. The detection of triptycene as evidence for the formation of benzyne was observed only in the decomposition of 2-(o-iodophenylazo)-2-propyl acetate in the p-xylene solution. The high yield of fluorobenzene in the decomposition in p-xylene demonstrates that elimination did not occur significantly. The apparent failure to eliminate a fluoride ion is consistent with Roberts' observation that fluorobenzene-<sup>(4)</sup>2-d when reacted with potassium amide in liquid ammonia exchanged the deuterium atom but failed to eliminate a fluoride ion.

It is apparent that in these decompositions in p-xylene, proton abstraction was occurring from one or

more of the other components in the reaction mixture and effectively competed with the elimination step at the carbanion. This proton source may be either the acetone or the t-butylacetate which were developed, although in low concentrations, in the decomposition reactions. Another possible proton source may have been a t-butanol impurity in the potassium t-butoxide catalyst. This possibility is believed to be less important than the earlier suggestion since the nmr spectra of the potassium t-butoxide in benzene solution failed to indicate a hydroxyl proton signal.

The relative rate of elimination is expected to follow the usual order of halide elimination,  $I > Br > Cl > F$ . The relative rate of proton abstraction vs. elimination, at the carbanion would determine the amount of benzyne formed. Therefore, the formation of benzyne would be expected to be most probable in the 2-(o-iodophenylazo)-2-propyl acetate decomposition. The formation and identification of triptycene only in the decomposition of 2-(o-iodophenylazo)-2-propyl acetate was consistent with the above relationship. Although the yield of triptycene was too low to permit isolation on a semimicro scale, it was collected by vapor phase

chromatographic fractionation of a small portion of the reaction mixture. The identity of the triptycene was established by comparison of the retention times and infrared spectra with those of authentic triptycene. Although the yield of triptycene in this reaction was low, it should be recognized that in more favorable circumstances the efficiency of anthracene as a trapping agent has not been high. Thus in a reported preparative scale, formation of triptycene from anthracene and (15) o-fluorobromobenzene the yield was only 28%.

In view of the above results, it appears that decomposition of an azoacetate such as o-iodophenylazo diphenylmethyl benzoate would present a more favorable system for the formation of benzyne.

## SUMMARY

Three unreported azoacetates were prepared and characterized: 2-(o-fluorophenylazo)-2-propyl acetate, 2-(o-chlorophenylazo)-2-propyl acetate, and 2-(o-iodophenylazo)-2-propyl acetate. The decompositions of the three 2-(o-halophenylazo)-2-propyl acetates in protonic and non-protonic media were studied. The yields of the halobenzenes produced in the aqueous decompositions were determined. The non-aqueous decompositions failed to produce an effective new route to benzyne. The failure to form benzyne is believed to be a result of proton abstraction occurring at a higher rate than halide elimination. A benzyne adduct was detected in a trace amount in the decomposition of 2-(o-iodophenylazo)-2-propyl acetate in non-protonic media.

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## VITA

The author was born in Battle Creek, Michigan on April 5, 1939. He attended University High School in Kalamazoo and graduated in 1957. He received a B. S. degree in chemistry from Western Michigan University in 1962. In September 1962, he entered graduate school at Western Michigan and in 1964 was appointed to a research fellowship on a project supported by the National Science Foundation.



APPROVAL OF EXAMINING COMMITTEE

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Date July 21 1966