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Thermal and photochemical decompositions of the chloride salt of ortho-diazoiumphenlyacetic acid

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UNION COLLEGE - GRADUATE STUDIES

Schenectady, New York

THE THERMAL AND PHOTOCHEMICAL DECOMPOSITIONS OF THE CHLORIDE
SALT OF ORTHO-DIAZONIUMPHENYLACETIC ACID

A thesis presented to the Committee on Graduate Studies
and the Department of Chemistry of Union College, Schenectady,
New York, in partial fulfillment of the requirements for the
degree of Master of Science.

by John Oliver Rosser *UC 1964 MS 1967*
"

By *John Oliver Rosser*
(Student's signature)

Approved by *Kevork V. Nahbedian*
Thesis advisor

Approved by *W. W. [illegible]*
Committee on Graduate Studies

Date *6/2/67*

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to Jack, Peter, and Jeffrey

ACKNOWLEDGMENT

I would like to express my appreciation to Dr. Kevork V. Nahabedian for his guidance and endless patience throughout the course of the project.

I would also like to thank Dr. Howard E. Sheffer for his advice and the use of his sample of indazole during the year.

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ABSTRACT

Ortho-nitro-phenylacetic was synthesized,^{3,4,5} diazotized,⁶ and subjected to thermal and photochemical decomposition.

Indazole is formed when the diazonium chloride salt was thermally decomposed in water. When carbon tetrachloride was used as a solvent, a lactone-like product was formed. When an excess of pyridine in carbon tetrachloride was used no decomposition took place.

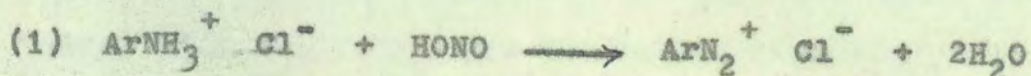
Photochemical decompositions using a mercury vapor lamp resulted in a combination of products when methanol was used as solvent and indazole when water was the solvent.

INTRODUCTION

When the chloride salt of o-diazoniumphenylacetic acid decomposes, the remote possibility exists that both nitrogen and carbon dioxide are evolved leaving as an intermediate benzocyclopropene. Because of this intriguing possibility, a study was made of the synthesis and decomposition of the hydrochloride of this diazonium salt. In carrying out this study, the diazonium salt was prepared starting with o-nitrotoluene and ethyl oxalate. Decompositions were carried out both thermally and photochemically.

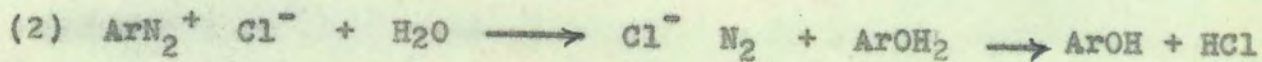
HISTORICAL

Diazonium salts were first prepared by Johan Peter Greiss in 1858 while working on a problem suggested by Kolbe. His initial synthesis was the reaction of nitrous acid with a salt of an aromatic amine:

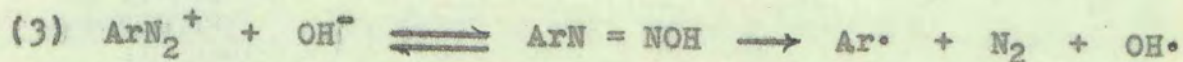


The importance of these compounds was soon recognized and within the course of the next five years, their reactions had been widely investigated. Azo dyes were soon developed and soon were being commercially produced. The investigations of the structure and reactions of diazonium salts have played an important part in the development of the theoretical aspects of organic chemistry.

These studies throughout the years have determined that there are two major mechanisms by which simple diazonium salts decompose. In acid medium, an ionic mechanism predominates:¹



In basic medium the Gomberg reaction can be expected to take place:²



The radicals formed take part in secondary reactions to form products that will vary with different solvents.

Most diazonium salts can be easily decomposed thermally.

The diazonium salt can be either suspended or dissolved in a solvent and the system refluxed. The amount of gas evolved can be determined indicating the extent of reaction. In this manner much has been learned concerning the nature and reactions of these compounds.

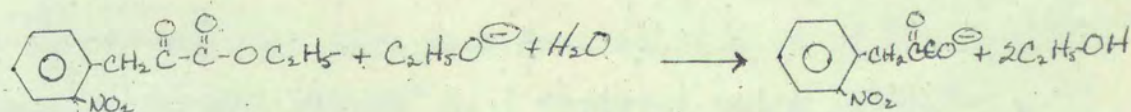
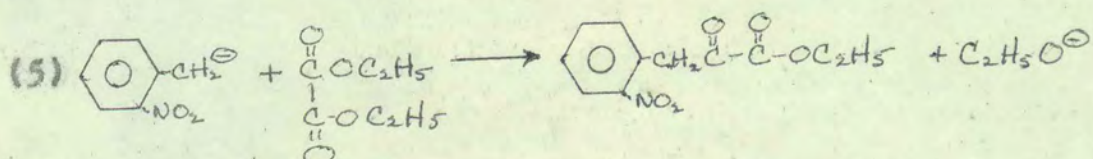
More recently, photochemical decompositions have come under investigation. The absorption of energy by molecules or atoms, which normally exist in a state of minimum electronic energy, the ground state, raises them to a less stable state of higher electronic energy, an excited state. Excited species can lose their excess energy by a variety of means. The most common of these are the emission of radiation and loss to the surroundings through collisions.

Each substance is selective in its absorption of radiation, depending on the presence of chromophores, which are atoms or functional groups which usually contain p electrons or π bonds.

The total energy of a chemical system consists of three components which are the following: rotational, vibrational, and electronic energies. The largest of these three energies is the electronic excitation energy. It is associated with the transition of electrons from their normal low-energy orbitals to orbitals of higher energy, and the excitation energy taken on by the molecule is of such magnitude as to be comparable to the bond energies. For this reason, many photochemical reactions can involve bond breaking.

EXPERIMENTAL

Ortho-nitro-phenylpyruvic acid was prepared by condensation of ethyl oxalate with o-nitrotoluene in the presence of sodium methoxide (all of which were purchased from Matheson, Coleman and Bell) using the method of E.L. May and E Mosettig.³ The reactions are shown in equations (4) and (5).



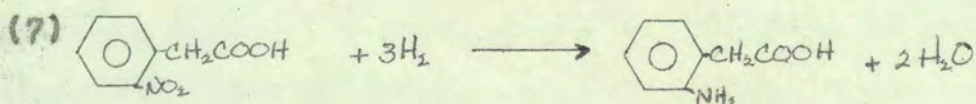
This substance was oxidized with hydrogen peroxide in alkaline solution to o-nitrophenylacetic acid (equation 6).



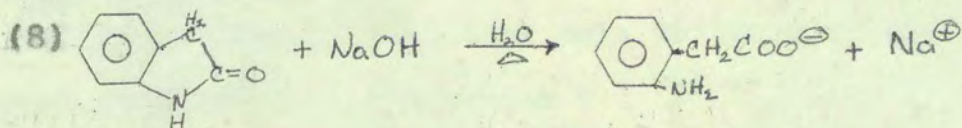
The product was obtained in a 60% overall yield and melted at 138-40° C after one recrystallization from water (norit). The reported value is 140° C.³

Ortho-aminophenylacetic acid was prepared by reduction of o-nitrophenylacetic acid in methanol with hydrogen and a

palladium-on-charcoal catalyst.⁴ (equation 7)



The product rapidly cyclizes to oxindole so that the re-crystallization from water (Norit) caused a substantial amount of oxindole to be formed. The resultant crystals, M.P. 117° C, were hydrolyzed using the method of De Martiis.⁵ (equation 8)



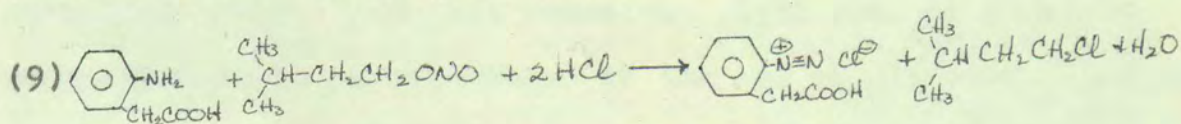
The amino acid resulting from neutrallization of the reaction mixture melted at 118-20° C. (reported value 119-20° C).⁴

The o-aminophenylacetic acid was diazotized using a method similar to that used by Stiles, Miller and Burekhardt.⁶ In the first diazotization, coded S-I, 1.55 gm (.013m) of the amino acid was dissolved in 18 ml. of ethanol (anhydrous), 1.2ml. (.014m) of concentrated hydrochloric acid was added, and the solution was cooled to 0° C. Three milliliters of isocamyl nitrite (.022m.), purchased from Matheson, Coleman and Bell, was slowly added and 18ml. of chilled anhydrous ether was added to precipitate the product, reddish-orange crystals that decompose at 245° C to a highly colored red liquid.

A Rast molecular weight determination was performed on this product and the resulting value for the molecular weight

was 157. A carbon, hydrogen, and nitrogen analysis showed 17.32%N, 57.90%C, 3.96%H, 20.82%O₂ + Silica, indicating an empirical formula of C₈H₆N₂O₂.

The second diazotization, coded S-II, was run in a similar manner using 2.3 grams (.015m) of amino acid in 23 ml. of anhydrous ethanol with (3cc) of concentrated hydrochloric acid (.036m). This solution was then treated with 3.75ml (.028m) of isoamyl nitrite. Twenty-three milliliters of chilled anhydrous ether was added and the results was the formation of pale yellow crystals that decompose at 95-105° C. (equation 9)



These products were thermally decomposed under varying conditions. In each case a Victor Myer apparatus was used to collect any evolved gas and this data is given in the following pages.

Thermal Decomposition I

Three tenths of a gram of the product from S-I was added to 25cc of carbon tetrachloride. This suspension was boiled at 76.8° C for one hour. At the end of this time, no gas had been evolved and the I.R. spectrum showed no change in the product.

Thermal Decomposition II

One tenth of a gram of the product from S-I was added to twenty-five ml. of distilled water and the system was refluxed at 100° C. The solid dissolved in the hot water but recrystallized at room temperature. After one hour, no gas had been evolved and the I.R. spectrum showed no change in the product.

Thermal Decomposition III

The product of reaction S-II was decomposed in boiling distilled water. For this reaction, .1542 gms. of crystals were added to 50 cc of water. At the end of one hour, 17.7 cc of gas had been collected. Theoretical yield is 18.50 cc on a mole for mole basis. The speed of the decomposition allowed a gas volume reading to be taken before the gas could dissolve to any extent in the water. The product obtained was a yellow oil which was soluble in ether. This oil dissolved in hot water and yellow crystals were formed upon cooling. These crystals (MP 143° C.) were analyzed for carbon, hydrogen, and nitrogen yielding the following results:

N= 23.00%, C= 70.20%, H= 5.15% other 1.65% (silica)

The empirical formula determined from this analysis is $C_7H_6N_2$ which is the formula for indazole. Comparative infrared spectra were run using a sample of indazole synthesized

from N-caproyl-o-toluidine and supplied by Dr. Howard Sheffer. The identical spectra with major peaks at 6.15, 6.65, 7.35, 10.55 and 11.75 microns prove that the decomposition product is indazole. Addition of silver nitrate to the solvent water of the decomposition shows a positive test for chloride ions thus showing that the product of reaction S-II is the chloride salt of o-diazoniumphenylacetic acid.

Thermal Decomposition IV

The product of reaction S-II was decomposed in refluxing carbon tetrachloride. Twenty-five milliliters of carbon tetrachloride were used to suspend .3498 gm of the diazonium hydrochloride salt. The reaction time was one hour. The amount of gas collected was 40.30 cc. The theoretical yield is 42.50 cc on a mole for mole basis. A yellow oil was present that was taken up in a mixture of benzene and petroleum ether. This solution was chilled and crystals were formed which melted at room temperature. When the solution was allowed to stand in the freezer for several weeks, crystals were formed that were stable at room temperature. These crystals were separated and the solvent was evaporated leaving a colorless oil. The crystals had a melting point of 68-70° and an infra-red spectrum showed major peaks at 5.55, 5.75 and 8.10 microns. These absorptions would be consistent with a lactone structure.

Thermal Decomposition V

In this experiment .0989 grams of the diazonium chloride salt was suspended in a mixture of 25 cc of carbon tetrachloride and .0750 grams of pyridine. The suspension was refluxed for one hour and no gas was evolved. When the solvent was removed, a yellow oil was left.

Eight milliliters of water was added to the flask containing the oil and was boiled. The oil was dissolved in the boiling water. Upon cooling, yellow crystals were formed and these were found to have an identical infra-red spectrum with the sample of indazole supplied by Professor Scheffer thus indicating that indazole is formed.

Thermal Decomposition VI

The diazonium chloride salt was allowed to decompose at room temperature. For this purpose, .1888 gm of the salt was added to 25 cc of water. The reaction produced a fine yellow precipitate. The infra-red spectrum showed that the product was indazole. The reaction evolved 14.2 cc (theory 22.8 cc) of gas over a 6 hour period indicating that a photochemical reaction could be run at room temperature without a high degree of thermal decomposition taking place.

The ultra-violet spectrum of the diazonium chloride was determined and found to have absorptions at 265 mu and 328 mu. With this information, a series of photochemical decompositions were carried out. The apparatus used was purchased from

Engelhard Hanovia Inc. and consisted of a quartz immersion well, a 450 watt high pressure mercury quartz lamp and a suitable power source. In all cases but Irradiation #3, the well was used in conjunction with a specially made reaction vessel that allowed the use of approximately 450 cc of solvent.

The chloride salt of o-diazoniumphenylacetic acid used for these irradiations was prepared using the same procedure as with S-II (excess acid procedure). In all cases, the solvent was bubbled thoroughly with nitrogen to remove all oxygen. A modified Victor Myer apparatus was used to collect the gas evolved.

Irradiation I

The diazonium chloride salt was decomposed using an ultra-violet light source. This apparatus comes equipped with various filters. In this experiment, a Vycor filter was used which cut out all light below 220 mμ from the reaction vessel. Four hundred and fifty milliliters of absolute methanol was used to dissolve .9834 gms of the diazonium chloride salt. The irradiation proceeded until no more gas evolved, (3.5 hours). The reaction well was placed in a dewar flask full of ice to start with but the sides of the flask reflected all of the light, melted the ice, and caused the water to heat up. The amount of water displaced was 185 cc (theory 123 cc.). The large excess of displaced water can

be attributed to thermal expansion. The resulting product, a brown gummy residue, was obtained by evaporation the solvent. It could not be crystalized from water and is unlike the product of the aqueous decomposition. Because of a shortage of time, this sample was not analyzed.

Irradiation II

The second irradiation was carried out at room temperature using the same apparatus as before. For this reaction .9766 gm of the diazonium chloride salt was dissolved in 450 cc of absolute methanol. The filter for this run was one made of pyrex that absorbs all light under 280 millimicrons. The irradiation was allowed to proceed for 1.5 hours at room temperature until no more gas was evolved. The total amount of gas collected was 114 cc (theory 117 cc). The solution was condensed by evaporation and distilled at reduced pressure. A clear, sweet smelling liquid came over at approximately 100⁰ C. leaving a dark gummy residue behind. The infa-red spectrum of the liquid shows a strong absorpction at 5.77 microns and moderate peaks at 8.60 and 8.80 microns indicating an ester, and peaks at 8.05 and 9.95 microns indicating an aromatic ether.

Irradiation III

Approximately .5 grams of the diazonium chloride salt was added to 50 cc of distilled water and the sample was irradiated at 4⁰ C for one hour, using the pyrex filter.

Sixty milliliters of gas was collected (theory 60 cc). A yellow oil was evident and that was extracted with ether. The solvent was evaporated and the resultant oil was taken up in hot water. Yellow crystals were formed when the water cooled and these were found to be indazole by comparing infrared spectra. A small tube was used rather than the regular reaction flask for this irradiation. For this reason, the photochemical decomposition was repeated (Irradiation IV) using the larger flask. This allows the immersion well containing the light source to be put into the reaction flask rather than next to it.

Irradiation IV

In this reaction, 1.8127 grams of the diazonium chloride was dissolved in 450 cc of distilled water. The reaction ran at room temperature for 1.5 hours and yielded 190 cc of gas (theory 221 cc). A yellow oil was evident and this was extracted with ether. This oil was dissolved in a minimum of hot water. Upon cooling, yellow crystals were formed which were found to be indazole by comparison of infrared spectra.

DISCUSSION OF RESULTS

The synthesis of o-nitrophenylpyruvic acid was accomplished by the condensation of o-nitrotoluene with ethyl oxalate in the presence of sodium methoxide as shown in equation (4) and (5). This product was finally oxidized to the o-nitrophenylacetic acid as shown in equation (6). Equation (7) shows the reduction of this product to the o-aminophenylacetic acid which tends to cyclize to oxindole. This latter compound was hydrolyzed back to the amino acid by the reaction in equation (8). This hydrolysis was carried out just before diazotization to limit the amount of recyclization occurring before the isoamyl nitrite could be added. During the course of this hydrolysis, the sample was stored in concentrated base for a period of time. It was here that the silica, reported in the carbon, hydrogen, nitrogen analysis, got into the sample. Qualitative evidence indicated that there was substantially more silica (about 10%) in the second product prepared by procedure S-II.

The diazotizations were carried out using two methods. The reddish-orange color of the product of reaction S-I would seem to indicate an azo compound. The high decomposition point (245°) and the fact that the decomposition product is more intensely colored, lend support to the theory that a high molecular weight azo compound is formed.

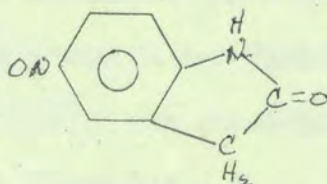
A Rast molecular weight determination was performed and the molecular weight was found to be 157. This would tend to

eliminate the possibility that a coupled product was formed because the carbon, oxygen, nitrogen analysis indicated a possible formula of $C_8H_6N_2O_2$. A greater than unit multiple of this formula would not coincide with the determined molecular weight.

A comparison of infra-red spectra of the product S-I and of oxindole indicate some significant similarities. These are at 1700 cm^{-1} (carbonyl absorbtion), and a doublet at 1100 and 1025 cm^{-1} in the C-N stretch region. The important differences occur at 1650 cm^{-1} , an absorption which is present in the S-I spectrum and indicates an unsymmetrically tri-substituted ring,⁷ and a peak at 1445 cm^{-1} , also in the S-I spectrum and which indicates the possibility of a nitroso function.

The structure for the presumed nitrosoxindole is shown as structure (10).

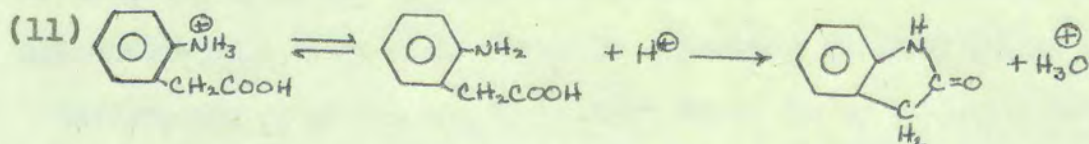
(10)



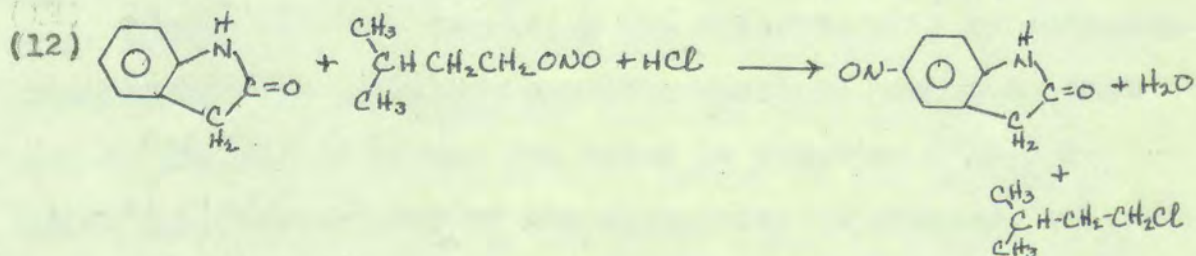
The molecular weight of the prosposed structure (163) would put it well within the limits of error for the Rast molecular weight determination.

The only difference between reaction S-I and S-II is the amount of concentrated hydrochloric acid used. In S-I the amount of acid used was approximately equimolar with the amino acid while in S-II an excess of acid was present. With this in mind, the changes shown in equation (11) can be set forth

as a possible explanation.



In a low acid medium (S-I) the second reaction in equation (11) might occur prior to addition of the iso-amyl nitrite which would then nitrosate the ring (equation 12).

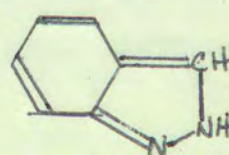
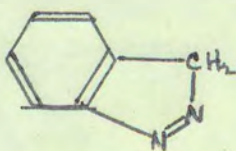
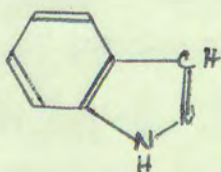


The likely position for the nitroso group would be para to the amide function of the oxindole. The ring activation by the N-H function should activate this position while the position ortho to the N-H would be sterically hindered.

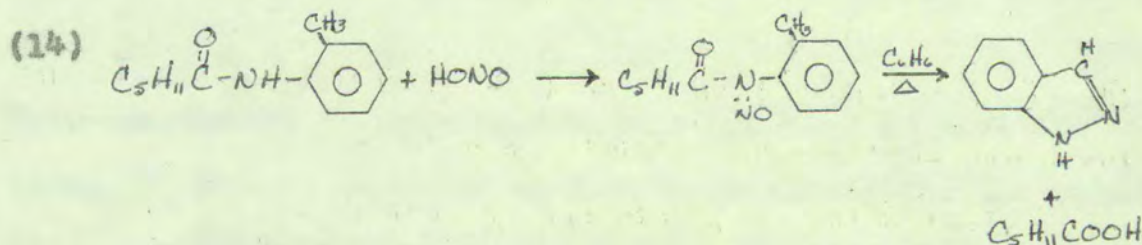
With an excess of acid, the reaction could be expected to proceed according to equation (9).

The product formed in this manner has been found to decompose in aqueous media to form indazole. This compound can exist in these following three forms:

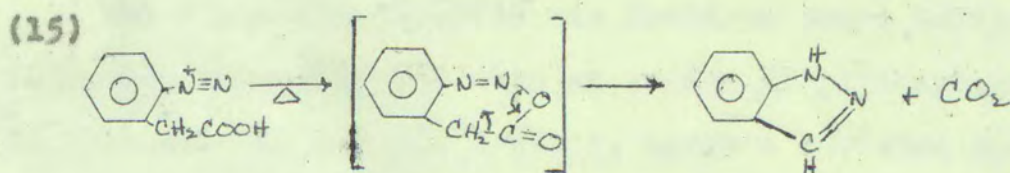
(13)



Several methods of indazol synthesis have been reported.⁸
The reference sample of indazole provided by Professor
Sheffer was made by the reaction shown in equation (14).



In the reaction involving the chloride salt of o-diazoniumphenylacetic acid, one possible reaction mechanism that can be postulated is the one shown in equation (15) in which the intermediacy of the diazoester is assumed, and the loss of carbon dioxide is assumed to occur simultaneously with the indazole ring formation.



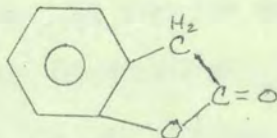
The concerted nature of the reaction is suggested by the fact that 3-carboxyindazole is very stable and melts at 260° with decarboxylation.⁹

The pale yellow color of the product can be attributed to an amount of azo coupling large enough to cause decolorization but so small as not to cause a significant difference in the infra-red spectrum.

The chloride salt of o-diazoniumphenylacetic acid was found to undergo a different reaction in carbon tetrachloride.

A possible lactone structure could be the following:

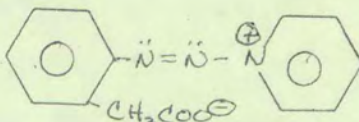
(16)



This substance, 2-oxo-coumarone, is reported to have two forms.¹⁰ One is unstable at room temperature and the other has a reported melting point of 49°. The fact that two forms exist is consistent with the observations made on the decomposition product but the reported melting point is much too low to allow an identification of the product as this material. Because of the small quantity of sample and the lack of time, no further analysis was performed on the compound.

The diazonium chloride was found to react differently in carbon tetrachloride when an excess of pyridine was added. In this case no gas was evolved, hence a compound such as the following must have been formed.

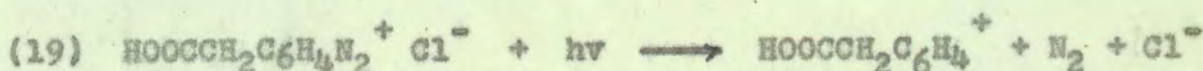
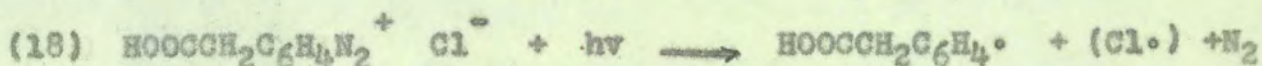
(17)



When the solvent was evaporated and boiling water added the presumed complex compound was broken down and the oil was dissolved in the hot water. Indazole was the resultant product.

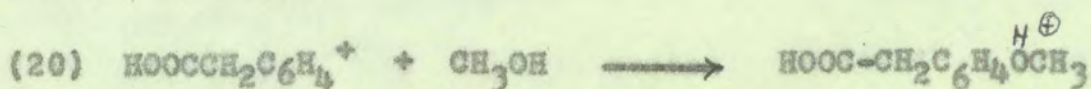
The photochemical reactions performed in methanol were

run with two different filters. In the first case (Ir-I) the vycor filter allowed a wider range of high energy light into the reaction flask. It can be speculated that the gummy residue from this irradiation represents a combination of products. Work done by Lee, Calvert and Malmberg suggests that in nonaqueous medium, radical reactions are a distinct possibility.¹¹ Their work, done on p-nitrobenzenediazonium chloride in ethanol, showed that two mechanisms were competing with one another. Using their work as an analogy, the two mechanisms occurring in this reaction can be assumed to be as follows:



Radicals from equation (18) could form numerous products through secondary radical reactions.

Reaction (19), which is of lower probability according to the reference, could be used to explain formation of an ether as follows:



The fact that a detectable amount of ester is formed in Irradiation II indicates that reaction (19) competes more

favorably than it did in Irradiation I. This indicates that the pyrex filter absorbed enough high energy so as to decrease the amount of radical formation.

In both the thermal and photochemical decompositions the amount of gas collected varied significantly from the theoretical amount expected. This must have been caused by thermal expansion of the gas or by dissolution of the evolved gas in water. For this purpose, the displacement of water was used as an indication of how rapidly the reaction was progressing but the amount of gas collected could not be considered quantitative.

SUMMARY

O-nitrophenylpyruvic acid was synthesized from o-nitrotoluene and ethyl oxalate in the presence of sodium methoxide. This product was then oxidized in basic medium to o-nitrophenylacetic acid which was reduced to the amino acid using hydrogen with palladium on charcoal as a catalyst. The amino acid was diazotized using approximately an equivalent amount of hydrochloric acid and the result was probably the formation of a ring nitrosated oxindole. The diazotization was also run using an excess of hydrochloric acid; the resultant product was the chloride salt of o-diazoniumphenylacetic acid.

The diazonium chloride salt decomposed thermally in water to form indazole. Thermal decomposition of this same salt in carbon tetrachloride produced a substance with a melting point of 68-70° that has infra-red absorption peaks similar to those of a lactone. Thermal decomposition in carbon tetrachloride with an excess of pyridine produced no gas. When the solvent was removed, the yellow oil that remained was dissolved in boiling water and indazole crystallized out when the solution was cooled.

Photochemical decompositions using a mercury vapor lamp, were run on the diazonium chloride salt. In the first case in methanol solvent, a Vycor filter was used and the resulting gummy residue was assumed to be a combination of products

from radical and ionic reactions. In the second case, also in methanol, a pyrex filter was used. The results were a small gummy residue and a clear, sweet smelling liquid which had an infra-red spectrum of an aromatic ring with both ether and ester substituents. The photochemical irradiations in water produced indazole.

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