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SECOND ANNUAL PROGRESS REPORT

December 15, 1980

and

SIX MONTHS PROGRESS REPORT

June 1, 1981

MONOMERS FOR THERMOSETTING AND TOUGHENING EPOXY RESINS

NSG-1539

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Department of Physical Sciences
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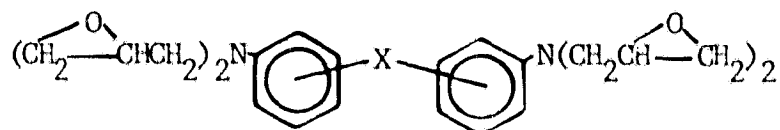
I. SIGNIFICANT RESULTS

1. Eight glycidyl amines have been prepared by alkylating the parent amine with epichlorohydrin to form the chlorohydrin, followed by cyclization with aqueous NaOH. Three of these compounds contained propargyl groups for postcuring studies.
2. A procedure for quantitatively estimating the epoxy content of these glycidyl amines has been employed for purity determination.
3. Two diamino carbonates and several model propargyl compounds were prepared. The synthesis of three new diamines, two which contain propargyloxy groups and another with a sec-butyl group, is in progress. These materials are at the dinitro stage now, ready for the final hydrogenation step.
4. Four aromatic diamines have been synthesized for mutagenic testing purposes. One of these compounds rapidly decomposes on exposure to air.

II. INTRODUCTION

The objective of the research conducted since the last One Year Progress Report (December 15, 1979) has been to synthesize and submit to Langley Research Center certain compounds from the following groups:

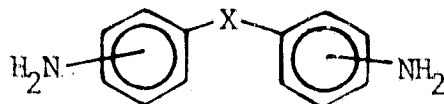
A. Glycidyl Amine Derivatives. Compounds having the following general structure, where X is $-\text{SO}_2-$, $-\text{CH}_2-$, and $-\text{CO}_3-$ and substituted



3,3'- and 4,4'- about the aniline rings, were needed for evaluating the effect of the X group on toughness in epoxy-graphite composites.

B. Propargyl-Containing Amines, Model Compounds, and Reactive Solvents. These compounds were needed to test the ability of the propargyl group to undergo a heat induced crosslinking or chain extension reaction when incorporated in various polymer systems such as polyamides or epoxides.

C. Compounds for Mutagenic Testing. Several aromatic diamines of the following general structure, where X is $-\text{SO}_2-$, $>\text{C}=\text{O}$, or $-\text{NH}-$ were



needed for evaluation as mutagenic agents. These compounds are part of a large series of compounds being evaluated by Monsanto Research Corp. for Langley.

Supplemental funding has recently been approved for the purchase of a Perkin-Elmer HPLC system composed of two pumps, a uv-visible detector, analytical and preparative columns, and a small printer-plotter. This instrument will be initially used for the analysis of the glycidyl amines

being prepared. We also plan to use this HPLC to monitor the purity of most compounds that are submitted to Langley.

Five students have worked as research assistants on grant projects. They have worked up to ten hours per week during both semesters of the school year or for ten weeks full-time during the summer. These students are Alice George, Laurie Gardiner, Jac Jonas, Jerri Elliott, and Alisa Williams. Jerri and Alisa have gone on to medical school, Alice has gone to graduate school (toxicology), and Laurie and Jac have gone to points unknown. Robin Ficklin began work several weeks ago as a summer research assistant.

III. RESULTS AND DISCUSSION

A. Glycidyl Amine Derivatives

As a result of recent dramatic increases in fuel prices, NASA has put research emphasis on the development of epoxy-graphite composite materials which have a high strength and improved toughness. These new materials may find use in second generation aircraft, whose chief feature will be reduced weight and improved fuel efficiency. One way to increase the toughness of epoxy resins may be to build into the epoxide monomer certain energy absorbing sulfone, carbonate, or carbocyclic groups. Thus, work under NSG-1539 is in progress to prepare certain tetraglycidylamines which contain these groups for evaluation in composites at Langley.

As will be explained in the following discussion, considerable initial difficulty has been experienced in preparing tetraglycidylamine compounds of 3,3'- and 4,4'-diaminodiphenyl sulfone with a high (e.g., > 90%) epoxy content. We believe that the problem may lie with the electron withdrawing nature of the sulfone group, as a similar preparation from 4,4'-methylenedianiline had an epoxy content of 89%. We feel that more strenuous reaction conditions during glycidation may be required. Preliminary experiments have shown this to be the case.

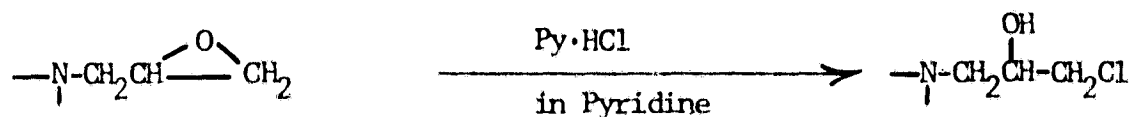
A second problem we encountered was in the measurement of the epoxy content. A titration method showing acceptable reproducibility has been developed from literature procedures, although this method gives slightly low values.

1. Quantitative Determination of the Epoxy Content

The epoxy content has been used to measure the purity of glycidyl amine derivatives. Briefly, the term epoxy content refers to the average number of epoxy groups contained in the average molecule of resin. Several procedures for its determination are known and have been reviewed.^{1,2}

We have used the pyridine hydrochloride in pyridine method. This method consists of adding a known excess of a standard pyridine hydrochloride

solution in pyridine to an accurately weighed sample (usually one gram) of the epoxy compound and heating. Most of the epoxy groups are converted to the chlorohydrin as in the following equation. The excess HCl is then



titrated with standard NaOH solution to a phenolphthalein end point. Calculation of the epoxy content is then made using the following equations.

$$\begin{array}{l} \text{no. equivalents epoxy} \\ \text{in compound} \end{array} + \begin{array}{l} \text{no. equivalents base} \\ \text{required to backtitrate} \end{array} = \begin{array}{l} \text{no. equivalents HCl} \\ \text{added as Py}\cdot\text{HCl in Py} \end{array}$$

From the definition of the equivalent weight (eq. wt.):

$$\frac{\text{sample size in of compound in grams}}{\text{eq. wt. of compound}} = \begin{array}{l} \text{no. of epoxy equivalents} \\ \text{in the compound} \end{array}$$

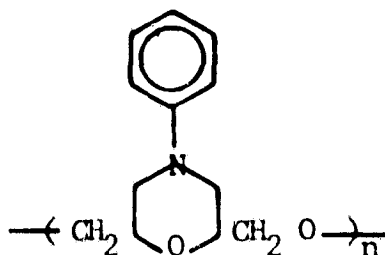
$$\text{epoxy content (in \%)} = \frac{\text{theoretical eq. wt.}}{\text{eq. wt. from titration}} \times 100$$

For example, an epoxy content determination (run in triplicate) was made on a sample of N,N-diglycidylaniline. This material, prepared over a year ago and freshly redistilled, gave the following analysis. See Experimental for details.

<u>Run no.</u>	<u>Epoxy Content, %</u>
1	95.3
2	90.4
3	92.5
average	<u>92.7</u>

The N,N-diglycidylaniline may not have been 100% pure, although the sample had been redistilled through a Vigreux column. This titration method is, in addition, known to give low epoxy content values.³ The formation of a small amount of a low molecular weight polymer having the

following structure during the reflux step with pyridine hydrochloride in pyridine is thought to be responsible for low epoxy content values.⁴



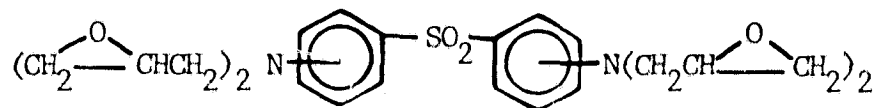
N,N-Bis(2,3-epoxypropyl)aniline

This compound was prepared in 72% yield from aniline and epichlorohydrin (molar ratio 1:4) followed by treatment of the resulting chlorohydrin with 50% aqueous NaOH. This compound was prepared as a model to determine suitable reaction conditions and infrared and NMR data for preparing and analyzing other compounds. In addition this compound was used as a standard to measure the accuracy and precision of the epoxy content determination previously discussed.

Several earlier attempts to prepare this compound using other experimental conditions were not successful. For example, the azeotropic removal of water during the NaOH cyclization step of the chlorohydrin of aniline led to the formation of excessive polymeric material in every case.

2. Glycidyl Sulfones, Methanes, and Carbonates

3,3'- and 4,4'-Sulfonylbis(N,N-bis(2,3-epoxypropyl))aniline



Both isomers were initially prepared using the procedure of Reinking.⁵ The tetrachlorohydrins were prepared from the diaminodiphenyl sulfones and excess epichlorohydrin in ethanol-water at 80°C, followed by cyclization with 50% aqueous NaOH and heat. The excess base was then removed by extraction into water, and a methylene chloride solution was dried before the solvent was removed in vacuo. Both compounds were light yellow, glassy solids at room temperature and required melting at a temperature of over 100°C before they could be poured. The analysis of these two isomers is

given in the following Table I.

Table I. Analysis of Glycidylamine Sulfones Prepared by the Procedure of Reinking.

<u>Isomer</u>	<u>Sample Size Submitted</u>	<u>% Yield</u>	<u>Epoxy Content, %</u>
3,3'-	157g	82	54*
4,4'-	162g	85	40

* Average of two analyses.

The literature reports the preparation of the 4,4'-isomer by the same general procedure but under different reaction conditions.⁶ The epoxy content varied between 61-68%, depending on the conditions.

The best explanation for the low epoxy content of these two sulfones appears to lie in the deactivating nature of the sulfone group on the amino group. This would appear to be especially important in the 4,4'-isomer, where inductive as well as resonance effects operate. More vigorous reaction conditions may be needed to fully alkylate these diamines with epichlorohydrin.

In this regard a modified procedure for alkylating highly hindered amines with epichlorohydrin has been found.⁷ For example, 2,4,6-tribromoaniline was converted to the corresponding N,N-diglycidylaniline derivative by heating the amine and epichlorohydrin with glacial acetic acid for 20 hrs. at 110°C. The epoxy content was 94.4%.

With this in mind we tried this modified procedure for the small scale preparation of the 4,4'-tetraglycidyl sulfone. We found that the epoxy content was increased to 50% by this modified procedure.

A second procedure has been suggested by R. Bauer of Shell Research and Development Corp.⁸ He recommended heating the reactants at 100°C for 20 hrs. and removal of the excess epichlorohydrin by distillation before cyclization with NaOH. An advantage to this procedure is that it may cut down on the amount of polymer formation (white powder) which is always observed during the cyclization step. Mr. Bauer claimed that NaOH easily opens and polymerizes epichlorohydrin.

We plan to continue small scale glycidation reactions with these sulfone diamines until we are able to produce a product having an adequate epoxy content.

4,4'-Methylenebis(N,N-bis(2,3-epoxypropyl)) aniline

This compound was prepared using a similar procedure to that of Reinking. Toluene was replaced by methylene chloride in dissolving the initial product. The epoxy content was found to be 89%.

3,3'-Methylenebis(N,N-bis(2,3-epoxypropyl)) aniline

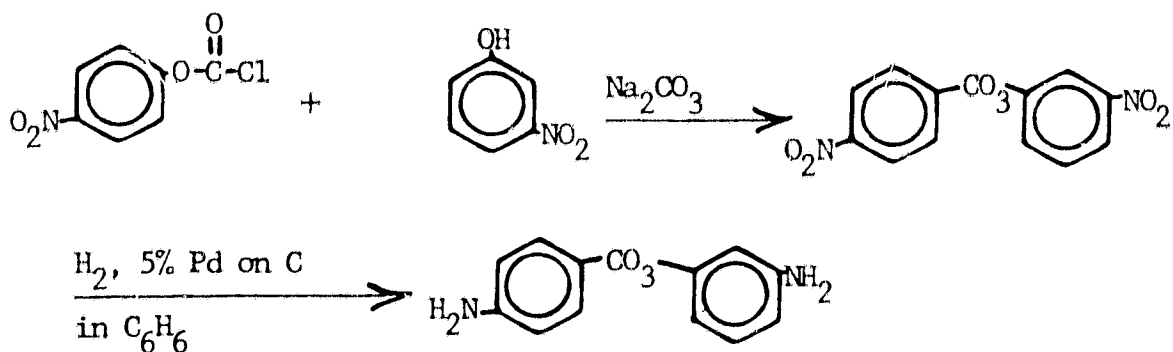
This compound was prepared on a smaller scale using the same procedure as in the previous example. However, the epoxy content, determined in duplicate, was much lower, 66.3 and 67.8%. Using the previously mentioned modified procedure (20 hrs. at 87°C), the epoxy content was 75.9 and 76.8%.

N,N'-Bis(2,3-epoxypropyl)-4,4'-trimethylenedipiperidine

Using a similar procedure as in the previous glycidyl compounds, a 2.5 g sample of this compound was prepared from 4,4'-trimethylenedipiperidine-epichlorohydrin and NaOH. The epoxy content was not determined.

3,4'-Diaminodiphenyl Carbonate

This new diamine was prepared as shown by reacting p-nitrophenyl



chloroformate with m-nitrophenol interfacially (methylene chloride-water) in the presence of sodium carbonate to remove the HCl produced. The resulting 3,4'-dinitrodiphenyl carbonate was then catalytically hydrogenated in a Parr hydrogenator with 5% Palladium on carbon. Seventeen grams of this material was submitted to Langley in three samples: 1.5 g, m.p. 107-109.5°C; 4.7 g, m.p. 112-113°C; and 10.8 g, m.p. 107-109°C. Melting was accompanied by decomposition and appeared to be sensitive to the rate of heating.

4,4'-Diaminodiphenyl Carbonate

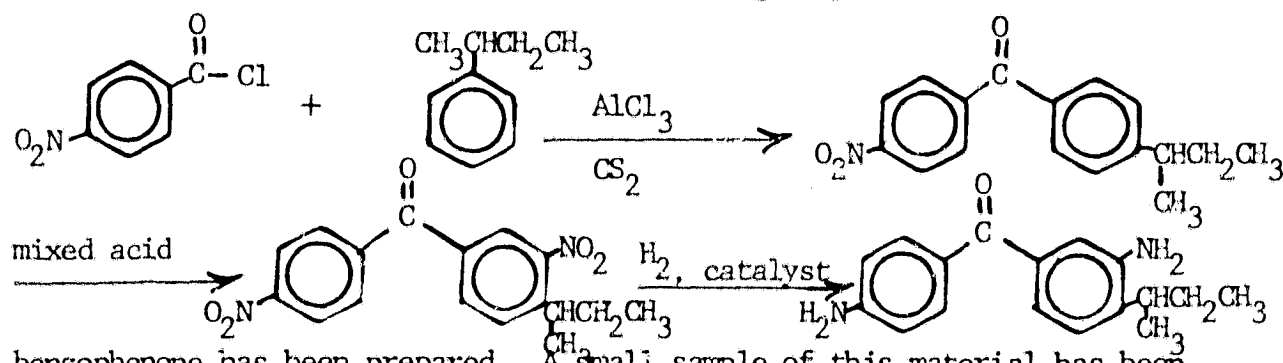
This diamine was prepared from p-nitrophenyl chloroformate and p-nitrophenol as in the previous example, followed by catalytic hydrogenation with

5% Palladium on carbon in benzene. Two samples of this material were submitted: 2.5 g, m.p. 145-147°C and 14.1 g, m.p. 147-148°C. As in the previous case, melting was accompanied by decomposition.

The preparation of a 100-200 g sample of both the 3,3'- and 4,4'-diamines is planned for this summer. Phosgene will be reacted with m- and p-nitrophenol in the presence of NaOH to form the corresponding 3,3'- and 4,4'-dinitrodiphenyl carbonates, which will then be hydrogenated to the diamines. These diamines will then be converted to their tetraglycidyl derivatives by previously mentioned procedures. The extent to which hydrolysis of the carbonate group will be a problem during the cyclization of the chlorohydrin with hot aqueous NaOH is unknown.

3,4'-Diamino-4-(2-butyl)benzophenone

This compound is being prepared as a special project for Brian Jensen as outlined below. To date a 60 g sample of the dinitro



benzophenone has been prepared. A small sample of this material has been successfully hydrogenated to the diamine.

B. Propargyl-Containing Amines, Model Compounds, and Reactive Solvents

The compounds discussed under this section were prepared under the following categories:

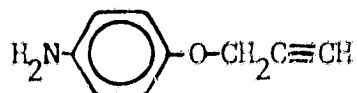
1. Amine and Glycidyl Amine Compounds Containing the Propargyl Group. The attempted preparation of four novel compounds (two were prepared) that contain both N-glycidyl and propargyl groups is discussed. The intent of this study was to prepare compounds for testing which could be copolymerized in epoxy systems and which can thermoset on postcuring.

2. Propargyloxydiamines. The attempted synthesis of two novel diamines that contain propargyloxy groups was made. The monomers can be

incorporated in postcurable amide polymers.

3. Miscellaneous Propargyl Compounds. These are all model compounds prepared for thermal analysis. One compound, N-propargyl-2-pyrrolidinone, was prepared for use as a reactive solvent; it could not be made in sufficient purity for study. A preliminary pyrolysis GLC study of phenyl propargyl ether is also discussed.

1. Amine and Glycidyl Amine Compounds Containing the Propargyl Group.
4-Aminophenyl propargyl ether

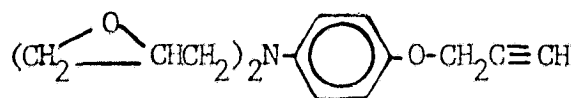


We originally prepared this compound in low yield by reducing the corresponding nitro compound with ferrous sulfate in ethanol. In an attempt to improve the yield and obtain a larger sample for testing, we tried several catalytic hydrogenations, summarized in Table II.

The attempted hydrogenation of 4-nitrophenyl propargyl ether using 5% Pt or Pd on carbon as the catalyst was not selective. Both acetylene and nitro groups were reduced. However, the use of Ru on alumina was made, following the recently reported procedure^{9,10} for reducing nitro compounds in the presence of acetylenes. Using this catalyst we were initially unable to separate product from byproduct by fractional crystallization. However, we were finally able to separate the amine by extracting its hydrochloride salt from the crude toluene filtrate with water. The aqueous layer was then neutralized with sodium bicarbonate to free the amine, which was extracted into benzene, dried, and distilled. The resulting colorless oil readily crystallized from methylene chloride-hexanes. The best yield to date has been 50%.

N,N-Bis(2,3-epoxypropyl)-4-propargyloxyaniline

This product was prepared twice by reacting the previously discussed



amine with epichlorohydrin at room temperature for 22 hours, followed by cyclization with aqueous NaOH and ethanol at reflux. The first product was

Table II. Results of Hydrogenation of
p-Nitrophenyl Propargyl Ether

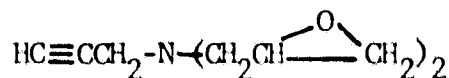
<u>Catalyst, Conditions</u>	<u>Results</u>
5% Pd on C in C ₆ H ₆ , 4 hrs. at 25°C	Complete reduction of both nitro and propargyl groups; isolated 4-propoxyaniline.
5% Pt on C, methanol, 3 hrs. at 25°C	Oily solid with broad m.p. Probably a mixture with both functional groups partially reduced.
5% Ru on Al ₂ O ₃ in C ₆ H ₆ , 4 hrs. at 25°C; catalyst/substrate ratio was 0.2 [*]	No uptake of H ₂ at 25°C; recovered starting material.
5% Ru on Al ₂ O ₃ , toluene, 30.5 hrs. at 71°C; catalyst/substrate ratio, 0.05 [*]	17% yield, 71% recovery of unreacted starting material.
5% Ru on Al ₂ O ₃ , toluene, 16.5 hrs. at 71°C; catalyst/ substrate ratio, 0.1 [*]	11% yield, 62% recovery of unreacted starting material.
5% Ru on Al ₂ O ₃ , toluene, 30 hrs. at 71°C; catalyst/substrate ratio, 0.2 [*]	50% yield

* Wt. of 5% Ru on Al₂O₃ in grams/ wt. of substrate in grams

distilled twice under vacuum without incident in 33% yield. However, a second scaled-up distillation exploded violently, destroying all of the undistilled material, spilling most of the distillate, and throwing glassware twelve feet into the air. No injury to personnel was received due to protection from a heavy Plexiglas shield. Approximately 2 grams of this compound was recovered and submitted to Langley.

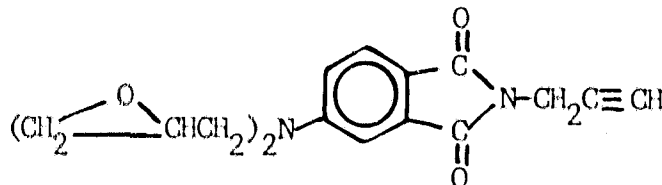
N,N-Bis(2,3-epoxypropyl)-2-propynamine

This compound was prepared by a similar procedure as in the previous example. Propargyl amine, epichlorohydrin, and NaOH were



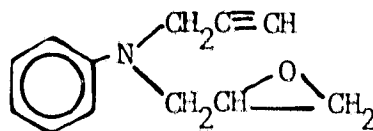
reacted and the product was distilled without incident. A 4.1 g sample of this material has been submitted.

N,N-Bis(2,3-epoxypropyl)-4-amino-N'-propargylphthalimide



Four attempts have been made to prepare this compound from the amine and excess epichlorohydrin, followed by cyclization with aqueous or ethanolic NaOH at temperatures from room temperature to that of refluxing toluene. In three cases a water soluble, viscous oil resulted, indicating that the imide ring had probably been opened. The attempted distillation of this oil in the fourth case led to severe decomposition of the product.

N-(2,3-epoxypropyl)-N-propargylaniline

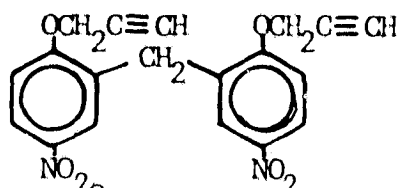


A 40 gram sample of N-propargylaniline was prepared by alkylating aniline with propargyl bromide in anhydrous acetone-potassium carbonate.

One attempt was made to alkylate this material with epichlorohydrin, followed by cyclization with ethanolic NaOH at 60°C. NMR analysis of the distillate (after fractionation three times through a 12-inch column) indicated that the product was primarily unreacted N-propargylaniline (78% recovery). This reaction needs to be rerun under more vigorous alkylation conditions. The hindered nature of the secondary amine apparently accounts for the difficulty of formation.

2. Propargyloxydianilines

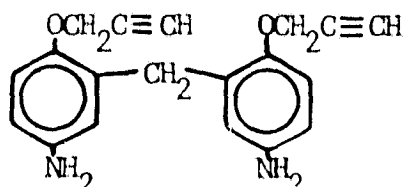
Bis(2-propargyloxy-5-nitrophenyl)methane



This compound, m.p. 208-211°C, was prepared from p-nitrophenol and formaldehyde solution in H₂SO₄ followed by alkylation of the resulting bisphenol with propargyl bromide-potassium carbonate in acetone in 79% yield (based on the bisphenol).

Bis(2-propargyloxy-5-aminophenyl)methane

Three attempts have been made to prepare this compound from the



corresponding dinitro derivative (above). The first attempted hydrogenation in THF using 5% Ruthenium on alumina at room temperature for 8 hours resulted in no hydrogen uptake and recovery of the starting material.

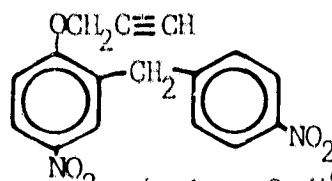
A second hydrogenation attempt was made with the same catalyst in benzene for 11 hours at 46-49°C and resulted in a 37% of theoretical uptake of hydrogen and a 64% recovery of starting dinitro substrate. No product could be isolated, and the remaining 36% of substrate could not be accounted for.

A third hydrogenation using the same catalyst in toluene was made; only a small amount of hydrogen was consumed at 71°C in 5 hours. A 43%

recovery of starting material was made. The remaining black solid dispersed in a colorless oil could not be crystallized. Infrared analysis of this material showed the presence of no acetylene or amine groups. However, nitro and ether groups were still present. This material did not melt below 260°C, which probably indicates polymer formation.

We did not try conventional hydrogenation catalysts such as Pt or Pd on carbon, due to their previously demonstrated nonselectivity in reducing both nitro and acetylene groups in a molecule. One additional hydrogenation is planned at 55-60°C, followed by extraction of any amine into dilute HCl, as was successfully used to remove 4-aminophenyl propargyl ether from starting material in a previous section. A ferrous sulfate reduction may also be attempted.

2-(4'-nitrobenzyl)-4-nitrophenyl propargyl ether



The starting dinitro substrate, 4-nitro-2-(4'-nitrobenzyl)phenol, was prepared by condensing p-nitrophenol with p-nitrobenzyl alcohol in conc. H_2SO_4 . Four attempts to alkylate this phenol with propargyl bromide and potassium carbonate in acetone have been made, and unreacted starting material has been isolated in each case. Another reaction is presently being run using higher boiling 2-butanone as the solvent.

3. Miscellaneous Propargyl Compounds

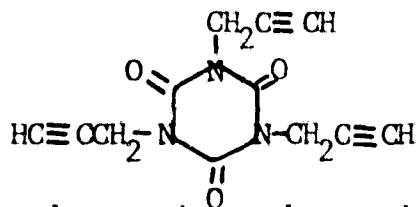
Pyrolysis Study of Phenyl Propargyl Ether

Several compounds that contain propargyl groups are known to undergo some kind of thermoset reaction; this reaction has been found by DSC to reach a maximum rate between 250-325°C. Volatiles are evolved during the cure. In an attempt to understand what compounds may be forming during pyrolysis, a sample of phenyl propargyl ether was heated with air one hour at 230-310°C in a sealed glass tube. The resulting tan oil showed at least three GLC peaks when chromatographed on a SE-30 column (225°C). One of these peaks was the starting material.

Two additional samples of this compound were sealed in vacuo in glass tubes and heated separately at 275°C in a silicone oil bath. After approximately three minutes, each sample exploded from excessive pressure build-up.

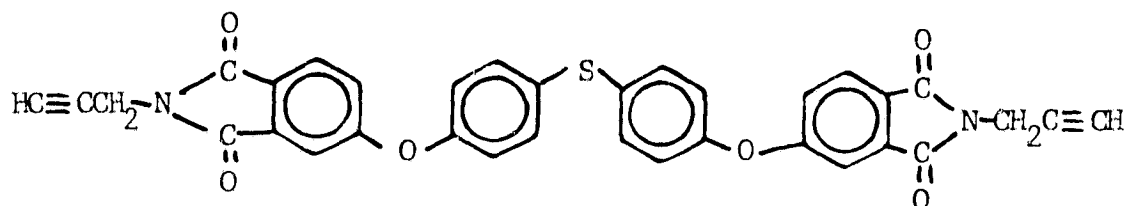
Tripropargyl-s-triazine-2,4,6(1H, 3H, 5H)trione

This model compound was prepared by alkylating cyanuric chloride



with propargyl alcohol and potassium carbonate in refluxing acetone. An analytical sample was examined by DSC and showed a strong exotherm maximum at 251°C.

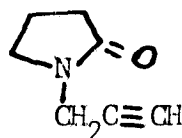
N,N'-Dipropargyl-4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfidediimide



Three attempts have been made to prepare this compound from the dianhydride and two moles of propargyl amine in refluxing glacial acetic acid. In each case a compound, m.p. 105-108°C (air dried), was initially isolated. After vacuum drying three hours at 87°C, the melting point fell to 92-98°C. Recrystallization from various solvent pairs led to further reduction and broadening of the melting point. The infrared(KBr) and NMR spectra showed the presence of the propargyl group. This infrared also showed strong imide absorption (1784 and 1716, doublet) and 1401 cm⁻¹. The infrared spectrum of the product was significantly different from that of the starting dianhydride.

A second method involved the attempted alkylation of the dipthalimide (prepared from the dianhydride and urea) with propargyl bromide-KOH in alcohol, and this also failed to give the desired product.

N-Propargyl-2-pyrrolidinone



Five attempts were made to prepare this compound for use as a

reactive solvent in polyimide synthesis. The initial attempts were made by treating 2-pyrrolidinone with KOH in methanol, azeotropically removing the water, and alkylation of the resulting anion with propargyl bromide. However, based on a literature¹¹ value of refractive index, a product of only approximately 79% purity was the best that could be achieved. The 2-pyrrolidinone impurity could not be removed by fractional distillation through a 12-inch glass column.

One additional attempt was made to prepare this compound by treating 2-pyrrolidinone with NaH in mineral oil, followed by alkylation with the propargyl bromide. However, the crude product (a red oil) polymerized to a rubbery solid on attempted distillation.

C. Compounds for Mutagenic Testing

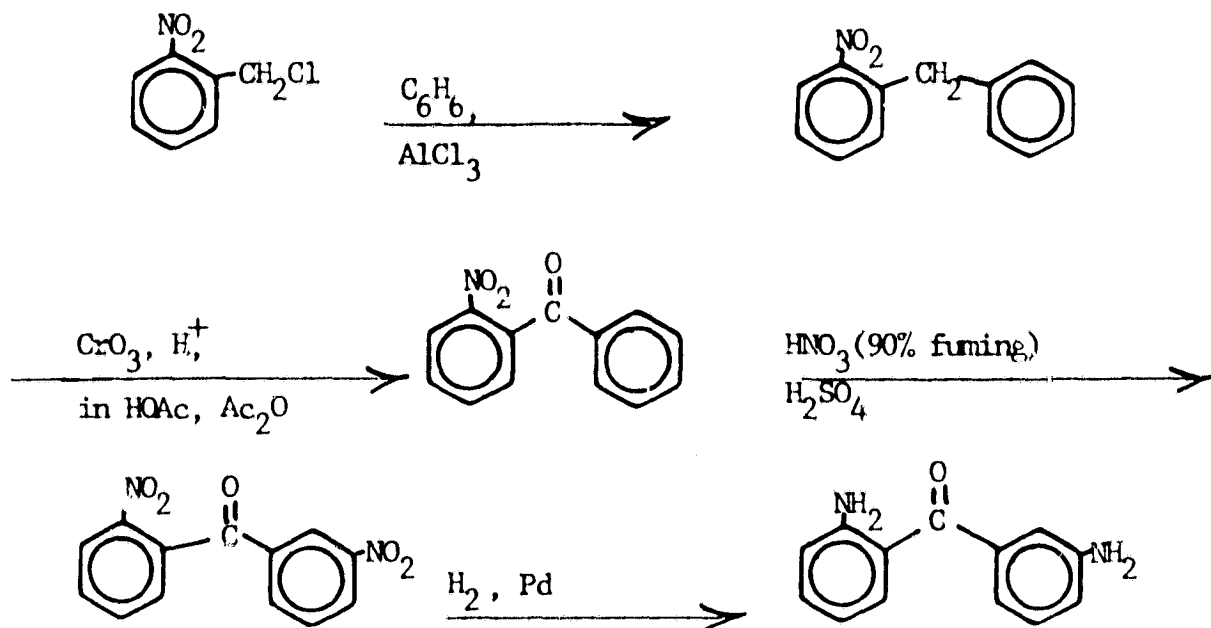
Several aromatic amines and diamines are known to be chemical carcinogens. Because of Langley's experience in the synthesis and polymerization of isomeric aromatic amines, they have undertaken a systematic study to assess the mutagenicity (and hence possible carcinogenicity) of several series of aromatic diamines.

We were asked to prepare small samples of five diamines for this study. To date, four of these compounds have been prepared and submitted. They are 2,3'-diaminobenzophenone, 2,3'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, and 2,4'-diaminodiphenylamine. This last compound was found to be unstable, hence the preparation of a larger sample is pending. The synthesis of the final compound, 2,2'-diaminodiphenyl sulfone, is in progress.

Because of obvious potential hazard in working with this group of compounds, we have tried to maintain adequate exposure safety precautions. Such precautions have included working in the hood with these materials (or their precursors) whenever possible, wearing of protective clothing and gloves, and adequate wash-up with strong detergent on leaving the laboratory.

2,3'-Diaminobenzophenone

As outlined below this compound was prepared with difficulty using procedures similar to those of Gager and Stump.¹² Because of problems with low yields, difficulties in purification, and expense of the starting o-nitrobenzyl chloride, each step in this reaction sequence required a number of small-scale reactions before scale-up was attempted.



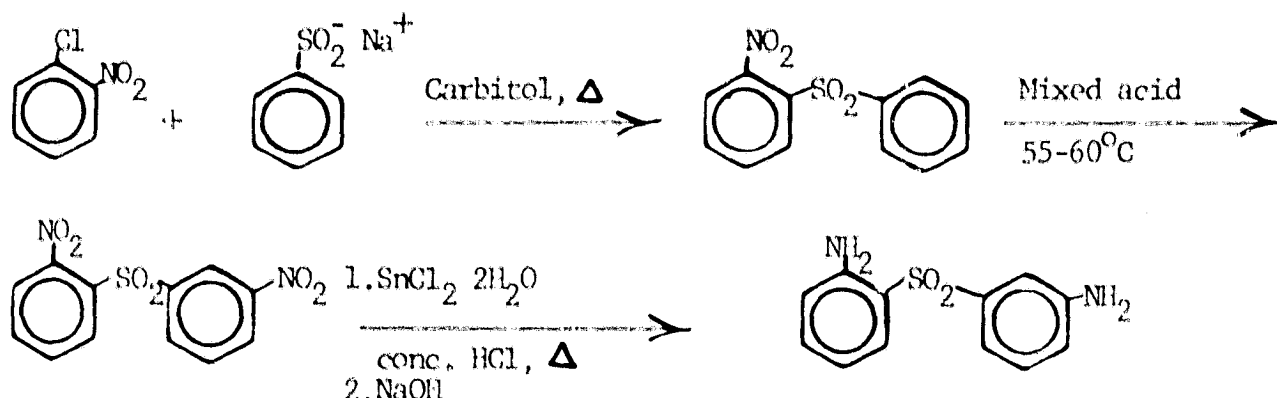
The first step involved the Friedel-Crafts alkylation of o-nitrobenzyl chloride and benzene to form o-nitrodiphenylmethane. This material could not be adequately purified by distillation; the impure pale orange distillate was collected and subjected to a chromium trioxide oxidation to form o-nitrobenzophenone. This material could then be recrystallized slowly from benzene. The direct preparation of this compound from o-nitrobenzoyl chloride and benzene (Friedel-Crafts) led to an oily solid which could not be recrystallized.

Nitration was then conducted using a large excess of 90% fuming HNO_3 in conc. H_2SO_4 at -4°C . The resulting 2,3'-dinitrobenzophenone was contaminated with higher melting by-products, probably the 2,2'- and 2,4'-dinitrobenzophenone isomers. Column chromatography on silica, although helpful, did not remove all impurities. Several recrystallizations from toluene appeared most satisfactory, giving a product which was approximately 96% pure as determined by HPLC.

Hydrogenation of 2,3'-dinitrobenzophenone with 5% Pd on Carbon gave the product, 2,3'-diaminobenzophenone, which showed a strong tendency to oil out of several solvents. A fine, pale yellow powder finally crystallized from a dilute solution of cyclohexane. On further standing for up to a week, this yellow powder was converted to off-white needles. Both crystalline forms had essentially the same melting point.

2,3'-Diaminodiphenyl Sulfone

This material was prepared according to the procedure of Baker, Kadish, and Querry¹³ as outlined below.



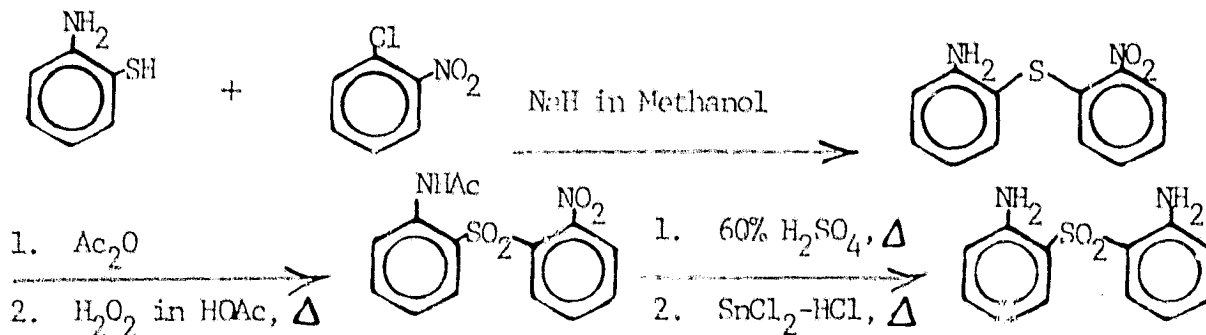
The sodium salt of benzenesulfonic acid was condensed with o-chloronitrobenzene in "Carbitol" (a high boiling ether of ethylene glycol) under a nitrogen atmosphere for 15 hours at 177°C. Considerable decomposition accompanied this reaction, and sublimation of the product was required to remove the dark brown color. The 2-nitrodiphenyl sulfone was nitrated with mixed acid at 55°C to 2,3'-dinitrodiphenyl sulfone, which was then reduced with SnCl_2 in conc. HCl and recrystallized from methylene chloride-petroleum ether to the product.

3,4'-Diaminodiphenyl Sulfone

This compound was prepared in a similar fashion as the previous isomer. The attempted catalytic hydrogenation of the 3,4'-dinitrodiphenyl sulfone with either 5% Pt or Pd on carbon led to incomplete uptake of hydrogen, probably because of catalytic poisoning by the sulfone. Stannous chloride was used to reduce this nitro derivative to the diamine.

2,2'-Diaminodiphenyl Sulfone

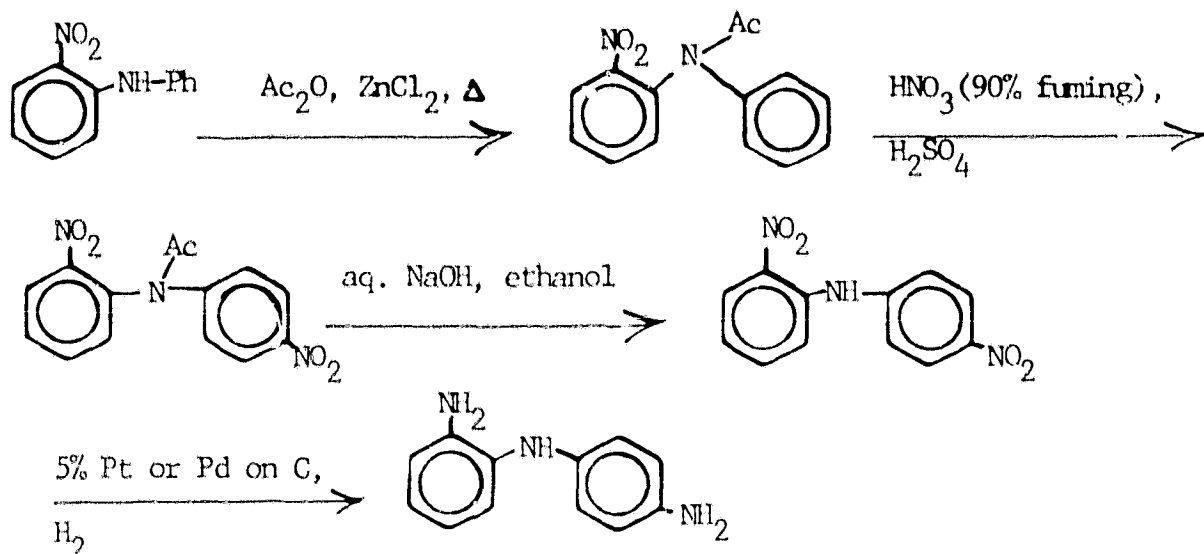
The following sequence of reactions is being used to prepare this material.^{14,15} To date only the first reaction has been run on a small scale.



A dispersion of NaH in mineral oil was used to form the sodium 2-aminothiophenoxide; this anion was then used to nucleophilically displace the chlorine in o-chloronitrobenzene to form the sulfide. A 78% yield of 2-amino-2'-nitrodiphenyl sulfide, m.p. 82-84°C, has been isolated. The literature reports m.p. 85°C.¹⁴

2,4'-Diaminodiphenylamine

The synthesis of this monomer is outlined below. A 56 gram sample of



2,4'-dinitrodiphenylamine has been prepared without difficulty. This bright orange solid melts at 223-224°C. Catalytic hydrogenation of this material with 5% Pt or Pd on carbon has been accomplished several times to afford off-white crystals of product. The best melting point achieved has been 53-54.5°C. Unfortunately, this material rapidly decomposes at room temperature on exposure to air. After storing for several days in a screw top vial, the original light pink solid had turned purple. After one or two weeks the sample had turned black and had begun to become oily in nature. After several weeks only a black oil remained. Dr. Bell is currently determining if this diamine can be used as prepared or if the dihydrochloride salt, a known compound, can be tested.

IV. EXPERIMENTAL

A. Glycidyl Amine Derivatives

1. Quantitative Determination of the Epoxy Content

The following example illustrates the determination of the epoxy content of N,N-diglycidylaniline. A standard pyridine hydrochloride in pyridine solution was prepared by adding 16.0 ml of conc. HCl to a 1 liter flask and diluting with 99+% pyridine to volume. The normality of this solution was found to be 0.1821 N by titration with standard NaOH solution to a phenolphthalein end point.

To a 0.96 g sample of N,N-diglycidylaniline was added 50 ml of the standard pyridine hydrochloride solution; the mixture was dissolved and then slowly refluxed for twenty minutes on the hot plate. After cooling 300 ml of deionized water and 10 drops of phenolphthalein solution was added. The solution was titrated to the first permanent pink color with 0.09375 N NaOH solution. A total volume of 4.8 ml of base was required. The pink color faded rather quickly due to reaction of the NaOH with CO₂ in the atmosphere. The calculations for the epoxy content were as follows:

$$\begin{aligned} \frac{0.96}{\text{eq. wt.}} + \frac{0.09375 (4.8)}{1000} &= \frac{0.1821 (50)}{1000} \\ \text{eq. wt.} &= 110.9 \text{ g/eq.} \\ \text{Epoxy Content} &= \frac{205.3/2 (100)}{110.9} \\ &= 92.5\% \end{aligned}$$

The low epoxy content was expected, as the method is known to give low results.^{4,8} In addition the substrate may not have been 100% pure. The N,N-diglycidylaniline used had been prepared a year ago and recently redistilled, b.p. 138-141.5° (0.40 mm), n_D^{23} 1.5649. The literature reports b.p. 130-133° (0.40 mm).¹⁶

N,N-Diglycidylaniline

A mixture of redistilled aniline (10.0 g, 0.107 mol) and epichlorohydrin (39.7 g, 0.429 mol, a 100% excess) was stirred at room temperature for 5 days. The pale yellow solution was rapidly mixed with 25.7 g of 50% aq. NaOH solution (a 50% excess) and 25 ml ethanol. A 15°C exotherm was noted. This mixture was refluxed for 4.25 hours. The volatiles were removed in vacuo and the resulting oil was dissolved in benzene and extracted with water four times. The benzene layer was dried with anhydrous $MgSO_4$ and the benzene was removed in vacuo. Two distillations (once through a 6-inch Vigreux column) gave the product, b.p. 131° (0.20 mm), n_D^{27} 1.5615. The yield after one distillation was 15.9 g (72%). The literature reports b.p. 130-133° (0.4 mm), 36% yield.¹⁶

2. Glycidyl Sulfones, Methanes, and Carbonates

3,3'-Sulfonylbis(N,N-bis(2,3-epoxypropyl))aniline

The procedure of Reinking⁵ was essentially followed to prepare this compound. 3,3'-sulfonyldianiline (100 g, 0.40 mol) and epichlorohydrin (628 g, 6.8 mol) were stirred in a three-neck, 3-liter flask equipped with a Trubore stirrer. Ethanol (520 ml) and water (80 ml) were added, and the contents was heated for four hours at 80°C. The temperature was reduced to 60°C and 160 g of 50% aqueous NaOH was added dropwise over a 3.5-hour period. After removal of a small amount of white polymer which formed during this cyclization step, the volatiles were removed on the evaporator and the resulting oil was dissolved in methylene chloride, washed four times with water, and dried over anhydrous $MgSO_4$. All volatiles were then removed for several hours on the evaporator at a temperature of up to 70°C, then 1.5 hours at 98°C until bubble formation ceased. On cooling the liquid solidified to a pale red, resinous material. The yield was 190.6 g (82%). The epoxy content was determined in duplicate and found to be 56.0 and 51.5%.

4,4'-Sulfonylbis(N,N-bis(2,3-epoxypropyl))aniline

A 162 g (85% yield) of this compound was similarly prepared and submitted to Langley. The epoxy content was 40%. In a modified procedure (21 hrs., 100°C in acetic acid) the epoxy content was 48.7 and 50.5% (av. 50%).

3,4'-Dinitrodiphenyl Carbonate

The reaction of p-nitrophenyl chloroformate (2.0 g, 0.010 mol) with m-nitrophenol (1.39 g, 0.010 mol) in a blender containing 25 ml of

methylene chloride and 100 ml of water (interfacial reaction) for three minutes afforded the product. After removal of the methylene chloride in vacuo and filtration, the yield of white solid was 2.56 g (85%), m.p. 117-119.5°C. Recrystallization from methylene chloride-petroleum ether (2:1) in the freezer gave a product with a m.p. 118.5-121°C.

Anal. calcd. for $C_{13}H_8N_2O_7$: C, 51.33; H, 2.65. Found: C, 51.24; H, 2.73%.

3,4'-Diaminodiphenyl Carbonate

A three gram sample of 3,4'-dinitrodiphenyl carbonate was hydrogenated in 160 ml of benzene with 0.3 g of 5% Pd on carbon in a Parr hydrogenator. After shaking 1.5 hours at room temperature, the catalyst was removed by filtration, and the small amount of water was removed by drying with anhydrous $MgSO_4$. The volume of the solution was reduced to 50 ml under the aspirator before petroleum ether was added. Crystallization afforded 1.55 g (64%) of product, m.p. 107-109.5°C.

Anal. calcd. for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.88; H, 5.00; N, 11.47%.

Ir(KBr): 3405, 3315, and 1610 (amine); 1758 and 1245 cm^{-1} (ester carbonyl). Nitro absorption was not present.

4,4'-Dinitrodiphenyl Carbonate

The reaction of 4-nitrophenol (24.2 g, 0.174 mol) and 4-nitrophenyl chloroformate (35.0 g, 0.174 mol) in the presence of sodium carbonate (9.2 g, 0.087 mol) in an interfacial reaction as in the previous example gave the crude product. This material was recrystallized from acetone to give 30.1 g (60%) of long white needles, m.p. 131-133.5°C. On further recrystallization from methylene chloride the m.p. was 141-143.5°C. Lit.¹⁷ reports m.p. 138-140°C.

4,4'-Diaminodiphenyl Carbonate

The catalytic hydrogenation of the above diamine (1.95 g) with 0.18 g of 5% Pd on carbon in benzene gave 1.21 g (78%) of light tan crystals after one recrystallization from benzene, m.p. 147.5-149°C.

Anal. calcd. for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95. Found: C, 63.88; H, 5.01%. The literature reports m.p. 140°C (with decomposition).¹⁸

4-(2-Butyl)-4'-nitrobenzophenone

The Friedel-Crafts acylation of sec-butylbenzene (93.2 g, 0.69 mol) and p-nitrobenzoyl chloride* (123 g, 0.66 mol) with anhydrous AlCl_3 (102 g, 0.76 mol, a 10% excess) in 100 ml of carbon disulfide at reflux for 1.5 hours followed by hydrolysis with conc. HCl and ice afforded a tan solid. This solid was slurried with aqueous NaOH at pH 12 to remove any unreacted p-nitrobenzoic acid. The filtrate was neutralized with HCl and the resulting product was washed with water and then air dried. One recrystallization from benzene-petroleum ether (2:1) at 0°C afforded 149.8 g (76%) of light tan product, m.p. $78-81^\circ\text{C}$.

Ir(KBr): 1651 (carbonyl); 1518 and 1350 cm^{-1} (nitro).

3,4'-Dinitro-4-(2-butyl)benzophenone

4-(2-Butyl)-4'-nitrobenzophenone (5.01 g, 0.0177 mol) was nitrated in a mixture of 30 ml conc. HNO_3 and 50 ml H_2SO_4 at 68°C for 20 minutes, then at 50°C for 100 minutes. The mixture was poured over crushed ice to afford an oil. After the ice had melted the mixture was extracted with methylene chloride and the organic layer was washed with water and dried with anhyd. MgSO_4 . The product was crystallized with difficulty from methylene chloride-petroleum ether at 0°C . After three crops a crude yield of 2.71 g (47%) of this material was collected. One recrystallization from methanol at room temperature gave pale yellow crystals, m.p. $125.5-127^\circ\text{C}$.

Ir(KBr): 1677 (carbonyl); 1539 and 1357 cm^{-1} (nitro). The ratio of the transmittance of nitro to carbonyl was much larger for this compound than for the starting material.

* Freshly prepared from p-nitrobenzoic acid and PCl_5 and distilled, b.p. $156-160^\circ\text{C}$ (aspirator).

B. Propargyl-Containing Amines, Model Compounds, and Reactive Solvents
p-Aminophenyl Propargyl Ether

p-Nitrophenyl propargyl ether (14.3 g, 0.081 mol) was dissolved in 250 ml of toluene at 71°C, and 2.85 g of 5% Ru on alumina was added. This mixture was hydrogenated for 25.5 hrs. at 71°C, adding hydrogen periodically as required. The catalyst was then removed by filtration, and the volume of the filtrate was reduced by about 50% on the evaporator. A small amount of black solid was removed by filtration after the filtrate had stood in the freezer overnight.

The toluene solution was next extracted three times with 110 ml of 1 N HCl, and the aqueous extracts were combined. This acidic solution of the amine hydrochloride was then neutralized to pH 7 with NaHCO₃, and the resulting amine was dissolved in methylene chloride before the solution was dried with anhydrous MgSO₄ and reduced in volume on the evaporator.

The product was then distilled using the distilling head as the only column, b.p. 116-119.5° (0.50 mm); the yield was 5.8 g (50%). Crystallization occurred in the freezer from methylene chloride-hexanes to yield a product, m.p. 50-51.5°C. The analytical and infrared data for this compound was reported in the One Year Progress Report, Dec., 1979.

N,N-Bis(2,3-epoxypropyl)-4-propargyloxyaniline

A mixture of p-aminophenyl propargyl ether (1.5 g, 0.010 mol) and epichlorohydrin (5.7 g, 0.062 mol) was stirred at room temperature for 22 hours. The solution was then brought to reflux and 1.23 g (0.031 mol) of NaOH in ethanol was added. Reflux was maintained for 3 hours before all volatiles were removed on the evaporator. The product was redissolved in benzene and filtered, washed five times with water, and dried with anhydrous MgSO₄, before the benzene was removed on the evaporator. The resulting yellow oil was carefully distilled, using the distilling head as the column. The first of two distillations afforded 0.88 g (33%) of product, b.p. 173-187° (0.20 mm). This material was then redistilled, b.p. 170-174° (0.10 mm).

Anal. Calcd. for C₁₅H₁₇NO₃: C, 69.48; H, 6.61. Found: C, 68.95; H, 7.35%.

A later fractionation of this compound (from another preparation) exploded about one-half through the distillation. The distilling head

and thermometer was blown about twelve feet into the air. Miraculously, only one glass receiving flask was broken, although much of the distillate was spilled and the undistilled material was charred. The explosion was probably due to overheating the pot during the distillation, as well as to the sensitivity of the molecule.

N,N-Bis(2,3-epoxypropyl)-2-propynamine

Propargylamine (3.0 g, 0.0545 mol) and epichlorohydrin (30.4 g, 0.326 mol) were mixed at room temperature for 2 hours and then refluxed 0.5 hours. Sodium hydroxide (6.54 g, 0.164 mol) in 100 ml ethanol was then added, and the mixture was refluxed for 3 hours. All volatiles were removed in vacuo, and the product was redissolved in benzene. The benzene solution was washed several times with water & dried with anhydrous MgSO_4 , and the benzene was removed in vacuo. The product was distilled twice; the final fractionation gave a b.p. $140-142^\circ$ (0.50 mm). The yield was 5.3 g (58%).

Anal. calcd. for $\text{C}_9\text{H}_{13}\text{NO}_2$: C, 64.65; H, 7.84. Found: C, 63.40; H, 7.99%.

Ir(neat): 3271 (strong singlet, acetylenic $\equiv\text{C-H}$), 2108 (weak, $-\text{C}\equiv\text{C}-$); 916, 854 cm^{-1} (strong, epoxy ring). Lines in the NMR were grouped together too closely for assignment.

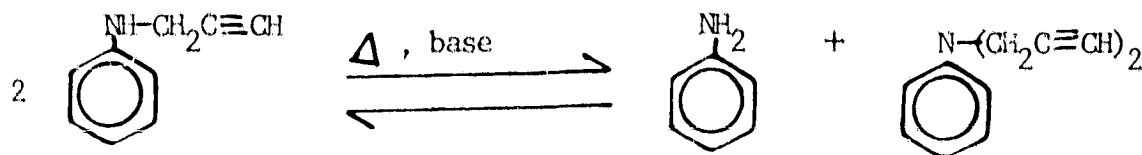
N-Propargylaniline

A mixture of aniline (76 g, 0.82 mol), propargyl bromide (121 g, 0.82 mol), and anhydrous potassium carbonate (113 g, 0.82 mol) was refluxed with 250 ml of anhydrous acetone for 72 hours. The solid was removed by filtration, and the volatiles were removed on the evaporator. The resulting tan oil was dissolved in methylene chloride, washed with water, and dried with anhydrous MgSO_4 . After removal of the methylene chloride in vacuo, the product was distilled to afford 40 g (37%) of N-propargylaniline, b.p. $94-95^\circ$ (0.15 mm), n_D^{25} 1.5723. The literature reports n_D^{20} 1.5772.¹⁹

N-Propargyl-N-(2,3-epoxypropyl)aniline

A mixture of N-propargylaniline (36.1 g, 0.275 mol) and epichlorohydrin (216 g, 2.33 mol) was heated with 195 ml of ethanol and 30 ml water for 4 hours at 30°C , according to the procedure of Reinking.⁵ The resulting chlorohydrin was then cyclized with aqueous NaOH at 60°C for 4 hours. Following the removal of all volatiles in vacuo, the resulting

oil was redissolved in methylene chloride, washed with water, and dried over anhydrous MgSO_4 . After removal of the solvent in vacuo, the product was distilled three times through a 12-inch glass column. The distillate, b.p. $118-120^\circ$ (0.70mm), $n_D^{22.5}$ 1.5659, contained no glycidyl compounds, as shown by NMR. It appeared to be essentially all starting N-propargylaniline (28 g, 78% recovery). Unfortunately, an NMR integration was not performed because of problems with the spectrometer. Based on a report by Wolf and Strauss,¹⁹ the recovered material probably was a mixture of N-propargylaniline and N,N-dipropargylaniline. They reported the following disproportionation reaction occurs when N-propargylaniline is heated with an organic base such as piperidine. The following analogous reaction probably occurred during the reaction with NaOH:



Bis(2-propargyloxy-5-nitrophenyl)methane

The alkylation of bis(2-hydroxy-5-nitrophenyl)methane, m.p. $260-263^\circ\text{C}$ (prepared from p-nitrophenol and formal solution in H_2SO_4),²⁰ with propargyl bromide and potassium carbonate in refluxing acetone for 47 hours gave a 79% yield of product, m.p. $208-211^\circ\text{C}$.

Ir(KBr): 3245 and 2110 ($\equiv\text{CH}$ and $-\text{C}\equiv\text{C}-$); 1480 and 1335 (nitro); 1250 and 1085 cm^{-1} (ether).

Bis(2-propargyloxy-5-aminophenyl)methane

Three catalytic hydrogenations with 5% Ruthenium on alumina have been run, all at different temperatures. Under the most severe reaction conditions a sample of bis(2-propargyloxy-5-nitrophenyl)methane (1.4 g) and 5% Ru on alumina (0.28 g) in 100 ml of toluene was shaken in a Parr hydrogenator for 5 hours at 71°C . The catalyst was removed by filtration, and the toluene was removed on the evaporator to afford a tan solid. Crystallization from acetone-hexanes (1:1) in the freezer gave 0.60 g (43%) of recovered starting material, m.p. $198-201^\circ\text{C}$. The infrared spectra of this material

and the starting dinitro compound were identical. When no further crystals could be obtained, the solvents were removed in vacuo to leave a black oily solid and a colorless oil.

Following the separation of the black oily solid from the colorless oil, an infrared spectrum of each was obtained. They appeared essentially identical. Ir(neat): 1460 and 1290 (nitro); 1270 and 1072 cm^{-1} . (ether). No absorption was observed at the 3100-3500 or 1580-1650 cm^{-1} (aromatic amine) range or 3270 and 2100 cm^{-1} (acetylene).

4-Nitro-2-(4-nitrobenzyl)phenol

The reaction of p-nitrophenol (29.1 g, 0.21 mol) and p-nitrobenzyl alcohol (32 g, 0.21 mol) in 120 ml conc. H_2SO_4 at room temperature for 24 hours afforded a black precipitate on pouring the solution into ice water. After thorough washing of this precipitate with water to remove the acid, it was recrystallized from acetone-water, then from methylene chloride to afford 19.2 g (33.5%) of product, m.p. 176-180°C.

Anal. calcd. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_5$: C, 56.94; H, 3.67. Found: C, 56.89; H, 3.80%.

Alkylation of 4-nitro-2-(4-nitrobenzyl)phenol with propargyl bromide

Three alkylation reactions were attempted. All three resulted in the recovery of unreacted starting material. For example, the reaction of 4-nitro-2-(4-nitrobenzyl)phenol (1.06 g, 0.0047 mol) with propargyl bromide (0.56 g, 0.004 mol) and K_2CO_3 (0.65 g, 0.0047 mol, a 20% excess) in 80 ml of refluxing anhydrous acetone for 48 hours gave a product with an identical m.p. as the starting material. This product showed no depression in melting on mixing with the starting material. Infrared and NMR spectra confirmed this result.

An additional attempt to alkylate this phenol in refluxing 2-butanone is now in progress.

Tripropargyl-s-triazine-2,4,6(1H,3H,5H)trione

The reaction of cyanuric chloride (17.7 g, 0.0960 mol) with propargyl alcohol (17.0g, 0.288 mol) in the presence of potassium carbonate (41.8 g, 0.288 mol) in 115 ml of anhydrous acetone was conducted for 21.5 hours at reflux under nitrogen. The resulting

slurry was stripped of most of the acetone and poured onto water to form a white mass of crystals, m.p. 67-70.5°C, yield, 11.4 g (48.8%). The filtrate containing additional product was discarded. After three recrystallizations from ethanol-water, benzene-hexanes, and methylene chloride-hexanes, the product had a melting point of 52-54.5°C and gave a positive Beilstein test for halogen.

However, two additional recrystallizations from acetone-hexanes and methylene chloride-hexanes gave the correct product, m.p. 76-78°C which gave a negative Beilstein test.

Anal. calcd. for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73. Found: C, 59.19; H, 3.73%.

Ir(KBr): 3246 and 2131 ($\equiv CH$ and $-C\equiv C-$); 1586 cm^{-1} (broad amide I band). NMR (CCl_4) showed only lines for the propargyl group.

N-Propargyl-2-pyrrolidinone

This compound was prepared according to the procedure of Bebbington and Shakeshaft¹¹ by treating 2-pyrrolidinone with KOH in methanol, removing of the water as an azeotrope, and reaction of the resulting potassium anion with propargyl bromide. However, an azeotrope composed of approximately 68% of the desired compound, based on refractive index, was the best that could be isolated. The other component was 2-pyrrolidinone. This mixture had a b.p. 144-145°C (33mm), n_D^{22} 1.4948. The literature reports n_D^{25} 1.4970.¹¹ The NMR showed a broad singlet at 7.5 δ (NH), confirming the 2-pyrrolidinone impurity.

C. Compounds for Mutagenic Testing

o-Nitrodiphenylmethane

o-Nitrobenzyl chloride (25 g, 0.146 mol) was reacted with 300 ml benzene (a large excess) in 100 ml carbon disulfide in the presence of 23.3 g of anhydrous AlCl_3 for 1.25 hours at 50°C . The product was poured onto ice, and the resulting organic and aqueous layers were separated. The organic layer was filtered to remove the AlCl_3 , washed once with water, dried, and stripped on the evaporator. The resulting dark brown oil was distilled twice to yield product of b.p. $108-111^\circ$ (0.05 mm), 21.9 g (70%), n_D^{20} 1.5983.

o-Nitrobenzophenone

A sample of o-nitrodiphenylmethane (21.9 g, 0.103 mol) was oxidized with chromium trioxide (52.3 g, 0.523 mol) in a mixture of 19.2 ml of conc. H_2SO_4 , 80 ml acetic anhydride, and 240 ml glacial acetic acid according to the procedure of Kovacs, et al.²¹ After 1.75 hours at a temperature of $10-20^\circ\text{C}$, the mixture was poured onto ice water, filtered, and slurried in water once before air drying. Fine white crystals were formed; the yield was 18.3 g (78%), m.p. $101.5-104^\circ\text{C}$.

2,3'-Dinitrobenzophenone

o-Nitrobenzophenone (18.2 g, 0.0802 mol) was dissolved in 20 ml conc. H_2SO_4 and cooled to 0°C . A mixture of 26 g of 90% nitric acid (yellow fuming) and 17.7 g of conc. H_2SO_4 was added dropwise over 1.3 hours, maintaining the temperature of the reaction generally in the 0° to -3°C range. At one point the temperature reached 9°C for a few minutes, as the reaction was quite exothermic during the early stage of the nitration. Ten minutes after the addition was complete the mixture was poured onto ice water to isolate tan crystals. After washing several times with water to remove the acids and after drying, this material had a melting point of $113-165^\circ\text{C}$. After one recrystallization from benzene-cyclohexane (2:1), the first crop (15.6 g, 71%) had a m.p. of $120.5-131^\circ\text{C}$, with a small amount of material unmelted. A second crop (2.5 g) melted at $119.5-159^\circ\text{C}$.

Numerous column chromatography experiments were performed on a 10-inch silica gel G column to attempt to purify this material. At least three bands were observed under a long wavelength uv lamp. One band appeared to

contain the higher melting dinitrobenzophenone isomer, m.p. 187.5-189°C. However, the major band was not fully resolved.

An 18 g sample of the crude 2,3'-dinitrobenzophenone was sent to Dr. Bell for sublimation. This material was instead recrystallized from toluene to remove much of the higher melting dinitro isomers.

Several sources of recrystallized 2,3'-dinitrobenzophenone were utilized in the final hydrogenation step. Some material had been recrystallized from toluene; other samples had been sublimed or recrystallized further from methylene chloride. A typical sample had a m.p. 124-126°C.

The sample which was recrystallized from toluene was found to be 96% pure by HPLC, yet DTA runs showed double peaks between 125-130°C. This phenomenon has not been explained but appears to involve a change in crystalline structure on melting.

2,3'-Diaminobenzophenone

A 7.3 g sample of 2,3'-dinitrobenzophenone was hydrogenated in a Parr hydrogenator for 1 hour with 1.81 g of 5% Pd on C in benzene. After removal of the catalyst and drying with anhydrous MgSO_4 , the solvent was removed in vacuo to afford a viscous oil. Crystallization was finally achieved from 1 liter of cyclohexane at room temperature after several days. A very fine, yellow powder, m.p. 75-78°C, was isolated. On standing for a day or longer these crystals appeared to reform, in part, as pale tan needles of identical melting point. In other cases this yellow powder formed an oil when disturbed. A total of 3.86 g of this diamine was submitted. The literature melting point is 76-78°C.¹²

2,3'- and 3,4'-Diaminodiphenyl Sulfone

These compounds were prepared using essentially the same procedures as in the literature.¹³ During the first step (condensation of sodium benzenesulfinate and o- or p-chloronitrobenzene in "Carbitol"), we found it very advantageous to run the reaction under nitrogen to cut down on a considerable amount of decomposition products observed when run in air. Both products were purified by repeated recrystallization (charcoal) and by sublimation to form pale yellow powders.

Both compounds were nitrated with mixed acid at 55-60°C, followed by stannous chloride reduction. The following table lists the melting points and sample sizes of materials which were submitted.

<u>Diamine isomer</u>	<u>m.p. (°C)</u>	<u>Sample Size Submitted</u>
2,3'-	124-126	12.3 g
3,4'-	129.5-132	4.5 g
3,4'-	129.5-133	2.7 g

N-Acetyl-2-nitrodiphenylamine

2-Nitrodiphenylamine (100 g, 0.47 mol) was stirred with 350 ml of acetic anhydride and 17.5 g of zinc chloride for 3.5 hours at 56-60°C. Water was then added dropwise (100 ml) over 15 minutes to control an exotherm. Additional water was then added more rapidly. The temperature of the reaction was not allowed to exceed 70°C. The solution was then cooled overnight at room temperature and then in the refrigerator for 5 hours before the product was filtered. The resulting solid was slurried in aqueous NaHCO₃, then with water before being dried. The resulting yellow powder (104 g, 87%) had a m.p. 133.5-135.5°C.

N-Acetyl-2,4'-dinitrodiphenylamine

N-Acetyl-2-nitrodiphenylamine (104 g, 0.407 mol) was dissolved in 300 ml conc. H₂SO₄ and cooled to -6°C in a ice-salt bath. The initial solution was dark black. A nitrating mixture composed of 180 g of 90% (fuming) nitric acid and 120 g of conc. H₂SO₄ was then added dropwise at an initial rate of approximately 1 drop/5-8 sec. Good stirring was maintained with a Trubore stirrer. The temperature was kept in the -6 to +1°C range. After the initial exotherm was complete and about one equivalent of the nitrating mixture had been added (about 80 minutes), the rate of addition was increased to 3 drops/sec. After all the acid had been added, the mixture was stirred for seven minutes longer at -8°C before it was poured onto 2.5 liters of ice water. A gray, gummy product was obtained. The aqueous acid layer was decanted and the oil was washed several times with water. The product was then dissolved in methylene chloride, and this solution was washed with aqueous NaHCO₃ and water before drying with anhydrous MgSO₄. On cooling in the freezer, three crops of product were isolated. The combined yield was 77.7 g (63.5%), m.p. 131-134°C.

2,4'-Dinitrodiphenylamine

N-Acetyl-2,4'-dinitrodiphenylamine (30.1 g, 0.100 mol) was dissolved in 600 ml of hot ethanol and 8.00 g (0.200 mol) of NaOH in 20 ml of hot water was added at once. The solution solidified rapidly as the product precipitated. More ethanol was added and the resulting solution was held at 50°C for 10 minutes before it was poured into water. The product was filtered and then slurried in water. The pH of this slurry was adjusted to about 7 with acetic acid, and the solid was filtered and dried. Recrystallization from dioxane at room temperature gave a 56.0% yield of product, m.p. 225-226.5°C. The literature reports m.p. 219.9-221°C.²²

2,4'-Diaminodiphenylamine

A sample of 2,4'-dinitrodiphenylamine (1.03 g, 0.0040 mol), 150 ml of benzene, and 0.11 g of 5% Pd on carbon was hydrogenated on the Parr hydrogenator for 2.25 hours. The theoretical amount of hydrogen uptake was measured. The catalyst was then removed by filtration, and the solution was dried with anhydrous MgSO₄ under sparging anhydrous nitrogen. Approximately one-half of the benzene was removed on the evaporator, and 20 ml of petroleum ether was added. After cooling in the freezer overnight, a small yield of product, m.p. 53-54.5°C, was obtained. The color of this product was initially off-white, but it rapidly changed to light pink on exposure to air. On storage in a screw cap vial for several days, the compound turned purple, then black. It finally became a black oil after several weeks.

The infrared (neat oil) showed a strong primary amine absorption at 3340 and 3225cm⁻¹ and a strong NH scissoring at 1615 and 1597cm⁻¹. It also contained absorptions in the aromatic nitro region which were considerably broadened over those of the starting material.

Another sample of the freshly prepared compound showed a broad, weak absorption in the 3350-3150 cm⁻¹ range, a strong NH₂ scissoring at 1592cm⁻¹, and no nitro absorption (other than a shoulder at 1513 cm⁻¹).

V. CONCLUSIONS

1. A series of glycidyl amines can be prepared in good yield, although with substantially less than the theoretical epoxy content.
2. A titration method for estimating the epoxy content of these glycidyl amines gives results approximately 7% low, \pm 2%.

VI. REFERENCES

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