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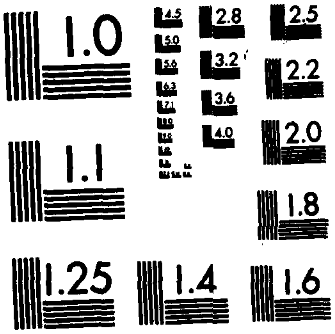

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Synthesis and Evaluation of New Intramolecular Cure Intermediates

Final Technical Report

AFOSR-82-0140

1 April ~~1982~~ - 30 September 1982

by

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Intramolecular Cure

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

The objectives of this research were the synthesis of 1,4,4,7-tetraphenylhepta-1,6-diyne-3,5-dione, 1,3,4,6-tetraphenylhexa-3-ene-1,5-diyne, 3-amino-2-(m-aminophenylethynyl)-N-phenylbenzamide and 4-amino-2-(m-aminophenylethynyl)-N-phenylbenzamide and their evaluation as potential intramolecular cure (IMC) agents.

The reaction of diphenylmalonyl dichloride with phenylacetylene in the presence of bis(triphenylphosphine)palladium(II)dichloride yields diphenylbutadiyne

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as the major product. The reaction of similarly substituted malonyl dichlorides with cuprous phenylacetylide yields only diphenylbutadiyne. The reaction of phenylethynylmagnesium bromide with substituted malonaldehydes followed by oxidation of the resulting diol to a diketone represents a better synthetic method if the malonaldehydes are available.

The reaction of 1,2-dibromo-1,2-diphenylethene or 1,2-diiodo-1,2-diphenylethene with phenylacetylene using bis(triphenylphosphine)palladium(II)dichloride as a catalyst or with cuprons phenylacetylide yields a mixture of diphenylacetylene and diphenylbutadiyne. The reaction of 3-bromo-1,3-diphenylpropyne with potassium tert-butoxide provided a highly fluorescent hydrocarbon which exhibits a DSC exotherm at 220°C (maximum) following a melt at 154°C. Characterization is incomplete.

Nitration of o-iodobenzoic acid provided 5-nitro-2-iodobenzoic acid which was converted smoothly to the N-phenylamide. Diazotization of 2-amino-4-nitrobenzoic acid provided 4-nitro-2-iodobenzoic acid which was also smoothly converted to the N-phenylamide. Coupling reactions of either of the above mentioned iodo compounds with m-aminophenylacetylene are anticipated to give the desired products.

I. Introduction

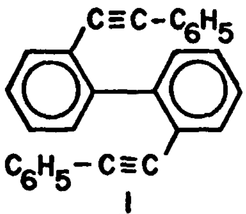
The motivation for this study is the current need for light-weight structural composite materials for use in advanced aircraft and aerospace vehicles.

State-of-the-art matrix resins, when used as structural composites, have considerable limitations. Aliphatic systems, for example epoxies, exhibit poor thermal oxidative stability and high moisture sensitivity both before and after cure. Aromatic and aromatic heterocyclic systems are generally not moisture sensitive but usually exhibit poor processing parameters and lack effective curing methods. In many systems, poor mechanical performance at high temperatures can be attributed to ineffective or incomplete curing.

Current methods of fabricating composites are based on the formation of intermolecular bonds. The resin must exhibit extensive flow to coat reinforcing fibers. Mobility is then decreased by a curing procedure involving reactive sites along the molecular chain providing a hardened, three-dimensional network. While intermolecular curing is used to decrease mobility, it is, at the same time, dependent on mobility for completeness. Thus the use temperature of one of these resins is only as high as the temperature used for curing - further softening and curing may occur at a higher temperature. Aromatic and aromatic heterocyclic systems are affected more than aliphatic systems because of their inherent rigidity. In addition, the three-dimensional networks considered here tend to be brittle and some may require condensation processes for intermolecular bond formation leading to evolution of volatile by-products and subsequent void formation.

The concept of an intramolecular cycloaddition or IMC cure has recently been advanced.[1] In this cure, mobility of a polymer chain, which exhibits the requisite flow and moldability, is decreased by having pairs of pendent groups along the polymer chain undergo an intramolecular cycloaddition reaction to form a more rigid, less mobile system. This type of reaction requires rotational movement of the polymer chain and therefore less mobility than that needed for intermolecular bond formation. The curing reaction can continue after the resin is "hard" and the use temperature should be substantially higher than the cure temperature. Further, a potentially brittle, three-dimensional network is avoided by the intramolecular cycloaddition as is the evolution of volatile void-producing by-products.

Intramolecular cycloaddition (IMC) cure has been demonstrated by using functionalized derivatives of 2,2-bis(phenylethynyl)biphenyl (1). An IMC reaction involving 1 yields 9-phenyldibenz a,c anthracene (2)[2,3] with no volatile by-product. In addition, the product is a fused aromatic structure which is thermal-oxidatively stable. When 1 was incorporated in the polyphenylquinoxaline (3), a 120 C advancement in T_g was observed which confirmed the basic premise of the IMC curing system.[4] Incorporation of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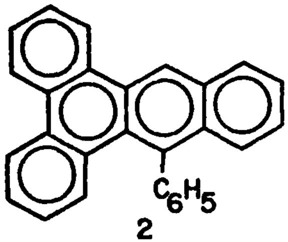
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1 in an aromatic polyimide[5,6,7] led to a similar substantial increase in T_g after cure.

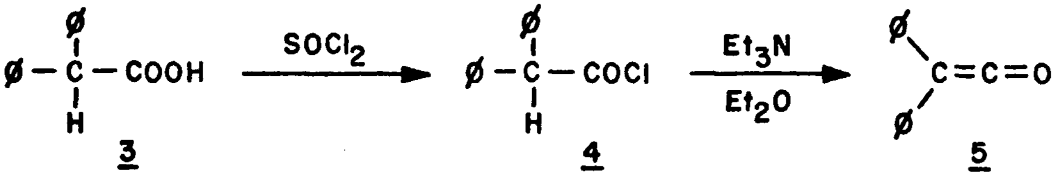
II. Objectives of the Contract

The objectives of this contract were: 1) the synthesis of 1,4,4,7-tetraphenylhepta-1,6-diyne-3,5-dione, 1,3,4,6-tetraphenylhexa-3-ene-1,5-diyne, 3-amino-2-(m-aminophenylethynyl)-N-phenylbenzamide and 4-amino-2-(m-aminophenylethynyl)-N-phenylbenzamide and 2) the evaluation of each of the above mentioned compounds as potential IMC curing agents by neat pyrolysis at or above the melting point and by pyrolysis in appropriate refluxing solvents.

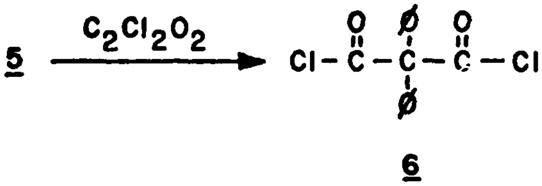
III. Work Performed

1) 1,4,4,7-Tetraphenylhepta-1,6-diyne-3,5-dione

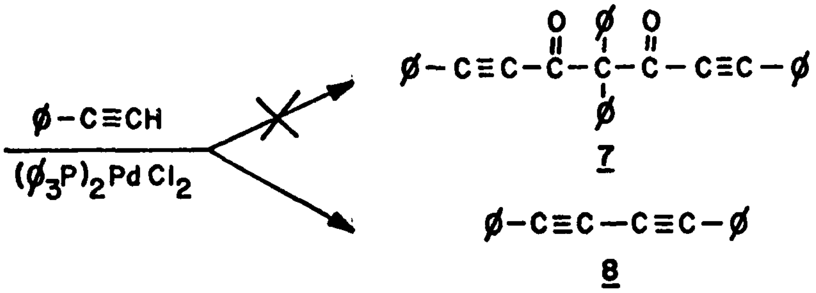
Diphenylacetic acid (3) was smoothly converted to diphenylacetyl chloride (4) with thionyl chloride. The dihydrohalogenation of 4 was carried out with triethylamine in ether to provide diphenylketene (5).[8]



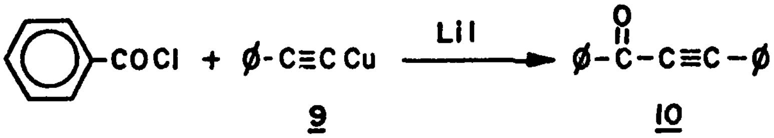
The reaction of 5 with oxalyl chloride[9] to produce diphenylmalonyl dichloride (6) appeared to be an equilibrium controlled reaction. The characteristic infrared absorp-

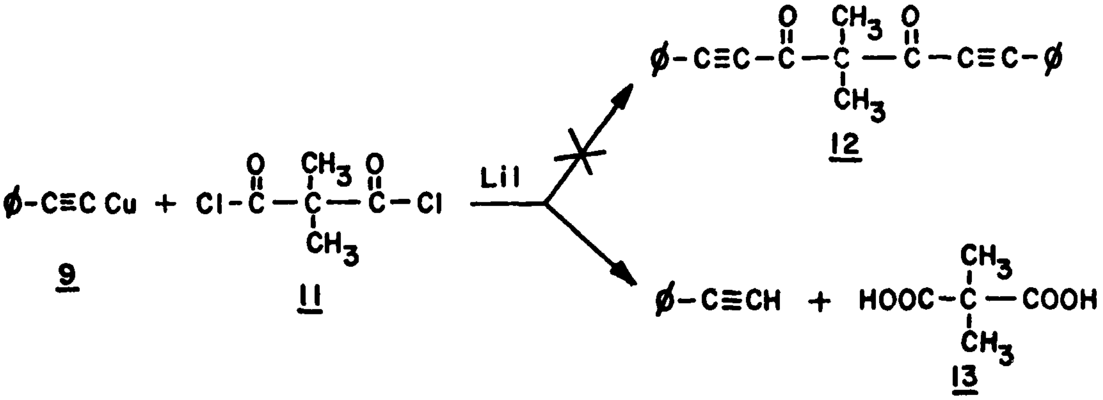


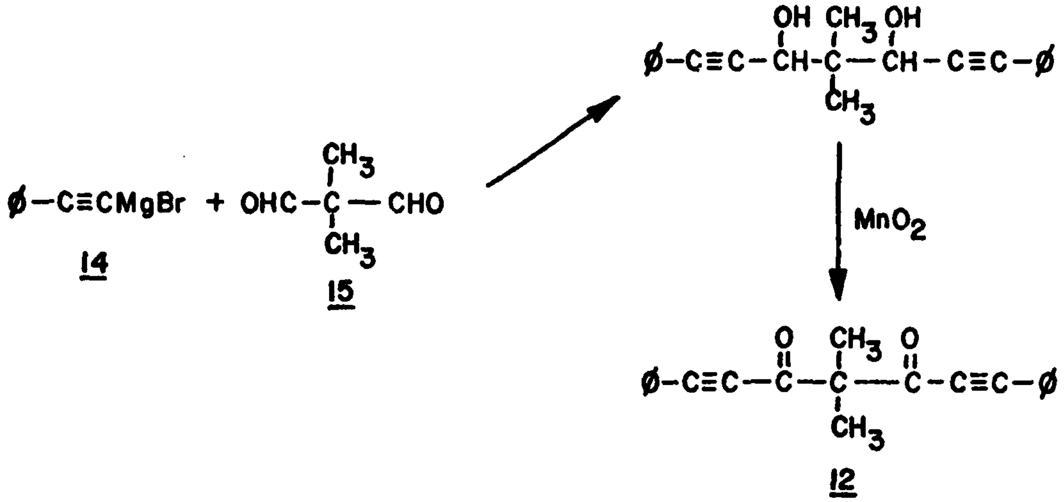
of diphenylketene at 2140 cm^{-1} was evident even after extended reflux times and the use of excess oxalyl chloride. Purification of <u>6</u> was tedious but could be accomplished by fractional vacuum distillation. The reaction of <u>6</u> with phenylacetylene in the presence of bis(triphenylphosphene)palladium(II) dichloride in refluxing triethylamine[10] was accompanied by the characteristic triethylamine hydrochloride precipitate but work-up of the reaction mixture provided only diphenylbutadiyne (<u>8</u>). The reaction was repeated at room temperature with identical results.



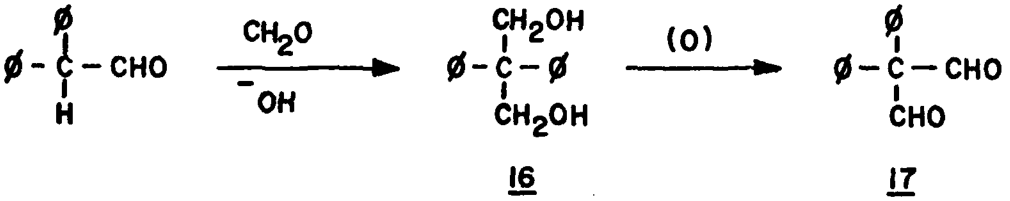
An alternate procedure, as suggested in the proposal, involves the reaction of cuprous phenylacetylide (<u>9</u>) with an acid chloride[11] like benzoyl chloride to yield phenylethynyl phenyl ketone (<u>10</u>). When this reaction was applied to dimethylmalonyl dichloride (<u>11</u>) (more accessable than diphenylmalonyl dichloride but similarly substituted) the only products isolated were phenylacetylene and dimethylmalonic acid (<u>13</u>) instead of 1,7-diphenyl-4,4-dimethyl-3,5-diketo-1,6-heptadiyne (<u>12</u>). An examination of the literature revealed that <u>12</u> had been previously synthesized by the reaction of phenylethynylmagnesium bromide (<u>14</u>) with dimethylmalonaldehyde (<u>15</u>).[12] Our current work on this part of the project involves the synthesis of <u>15</u> and/or





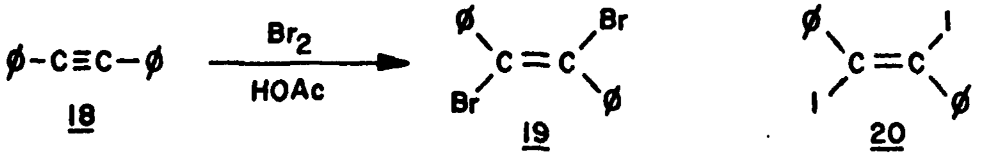


diphenylmalonaldehyde (17) by way of the diol 16.[13] We are concentrating on the synthesis of 12, 17 or a related similarly substituted system to test this IMC concept.

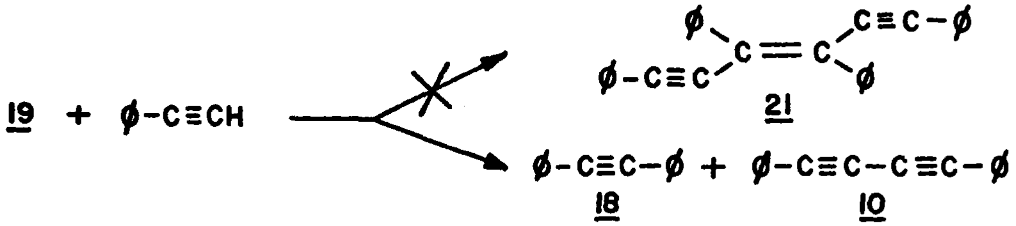


2) 1,3,4,6-Tetraphenylhexa-3-ene-1,5-diyne

The reaction of diphenylacetylene (18) with bromine in acetic acid[14] provided trans-1,2-dibromo-1,2-diphenylethene (19). Likewise, trans-1,2-diiodo-1,2-diphenylethene (20) was obtained, albeit at a slower rate, by reacting iodine with 18 in acetic acid.



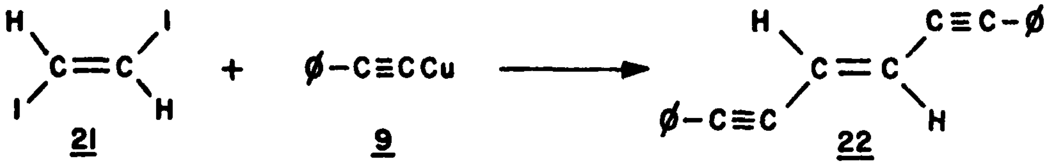
A series of reactions between 19 and phenylacetylene in triethylamine catalyzed by bis(triphenylphosphine)palladium (II) dichloride was carried out using conditions previously employed for other vinylic halide-acetylene couplings.[15]

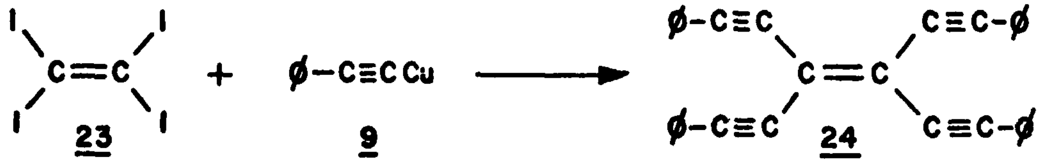


In each case the anticipated triethylamine hydrobromide was present but the product consisted of a mixture of diphenylacetylene and diphenylbutadiyne (8), the oxidative coupling product of phenylacetylene debromination of 19 occurs at the same time as oxidative coupling of pehnylacetylene and appears to be related to the presence of the catalyst. The products were identified by hydrogenation followed by gas chromatographic comparison to authentic standards.

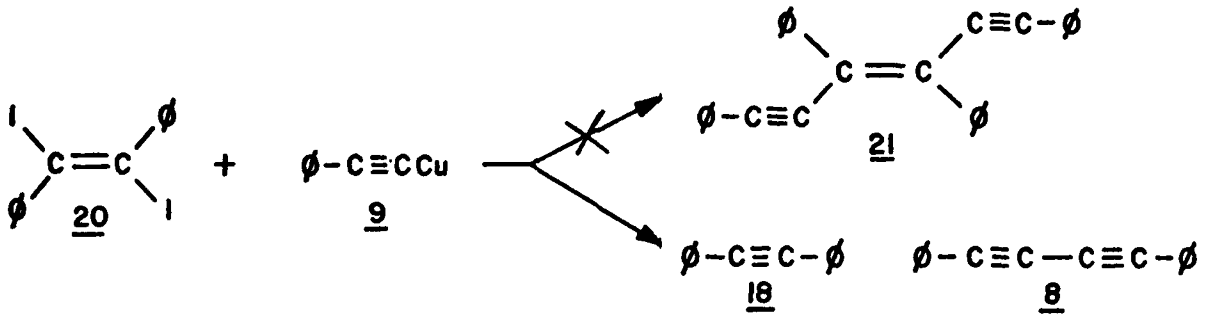
It was anticipated that the diiodo compound 20 would be more reactive on the basis of related coupling reactions involving iodoaromatics.[15] However, an identical product mixture was obtained (diphenylacetylene, diphenylbutadiyne) in a similar series of reactions in triethylamine employing bis(triphenylphosphine)palladium(II) dichloride as catalyst.

Organocopper reagents have also been reported to react with vinylic iodides.[11] For example, phenylethynyl copper(I) (11) reacts with trans-1,2-diiodoethylene (21) to reportedly yield *trans*-1,6-diphenylhex-3-ene-1,5-diyne (22)[16] and tetraiodoethylene (23) reportedly reacts with 9 to yield 1,6-diphenyl-3,4-bis(phenylethynyl)hex-

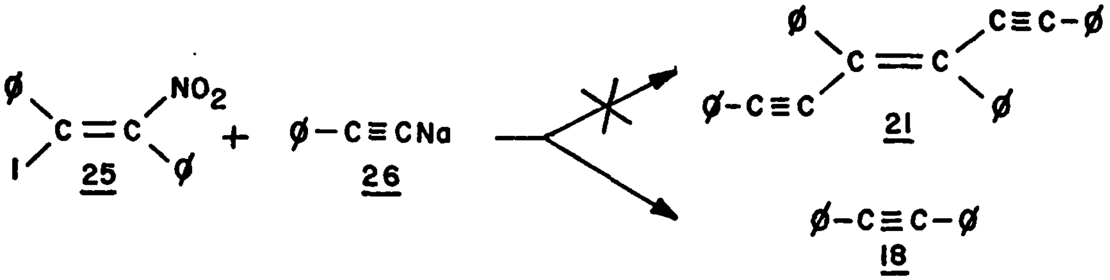




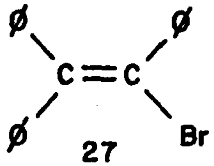
3-ene-1,5-diyne (24). When 20 was reacted with 11, the products isolated were diphenylacetylene and diphenylbutadiyne which were identified as earlier described. In view of our results, the reported synthesis of 24 appears, from physical properties and related characterization information, to be in error and the product is



actually diphenylbutadiyne (8). In addition, the reported synthesis of 21 by the reaction of trans-2-iodo-1-nitro-1,2-diphenylethylene (25) with sodium phenylacetylide (26) also appears to be in error[17] and diphenylacetylene is the most likely product.



These reactions all indicate the tendency of the dihalodiphenylethylenes 19 and 20 to undergo halogen elimination rather than the expected coupling. This behavior is best attributed to a steric effect coupled with a facile elimination pathway. Vinylic halides like bromotriethylethylene (27) couple successfully due to the lack



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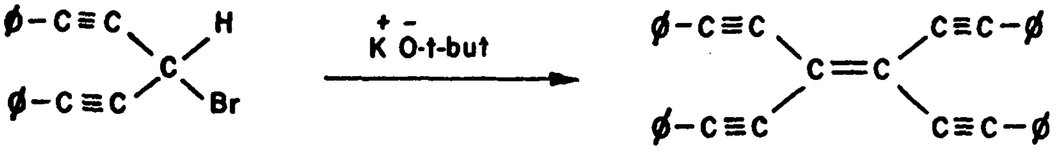
of an elimination possibility. In each of the coupling reactions described, diphenylbutadiyne (8) was a prominent product. It s presence was not unexpected as it is a known byproduct in palladium catalyzed reactions[15] and in the use of phenylethynyl copper(I).[18]

Our most promising research effort on this part of the project involves the synthesis of 21 by non-organometallic methods.

Hori, et. al.[19] reported the synthesis of 24 and two other isomers by the reaction of 1,5-diphenyl-3-bromo-1,4-pentadiyne (28) with potassium tert-butoxide. Complete identification of the products employed hydrogentation coupled with unequivocal syntheses. The reaction seems to be best explained as a carbene dimerization.



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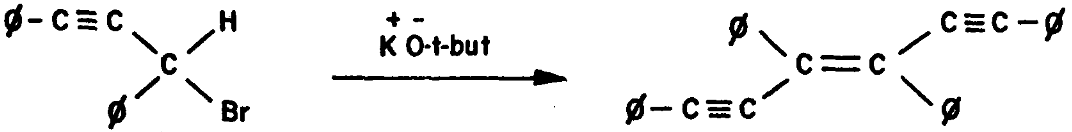
It seemed reasonable that a similar reaction employing 3-bromo-1,3-diphenylpropyne (29) should provide 21 as the only isomer because of the lack of rearrangement



29 21

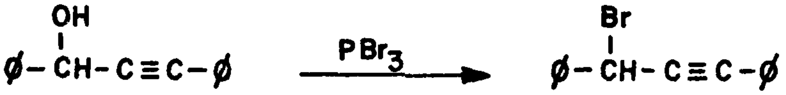
possibilities for the intermediate.

The reaction of phenylethynylmagnesium bromide (30) (prepared from phenylacetylene and ethylmagnesium bromide) with benzaldehyde^{20} provided 1,3-diphenyl-2-

$$\phi-C\equiv CMgBr + \phi-\overset{O}{\overset{\|}{C}}-H \longrightarrow \phi-\overset{OH}{\overset{|}{C}}H-C\equiv C-\phi$$

30 31

propyn-1-ol (31). The alcohol 33 was converted, on reaction with phosphorus tribromide, to 29.^{21} The NMR spectra of 31 and 29 are shown in Figures 1 and 2, respec-



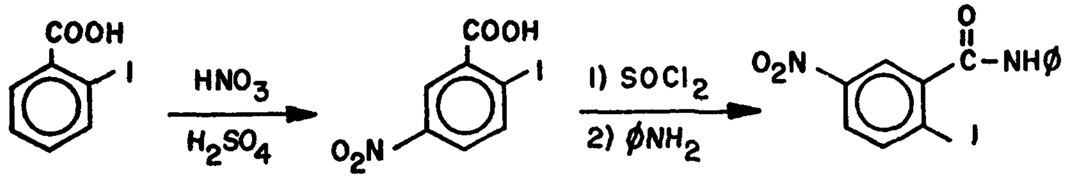
$$\phi-\overset{OH}{\overset{|}{C}}H-C\equiv C-\phi \xrightarrow{PBr_3} \phi-\overset{Br}{\overset{|}{C}}H-C\equiv C-\phi$$

31 29

tively. The infrared spectra of 31 and 29 are shown in Figures 3 and 4, respectively. When 29 was reacted with potassium tert-butoxide in THF/NMP, a complex product mixture was obtained from which a highly fluorescent hydrocarbon of mp 154°C was isolated by column chromatography on silica gel using hexane as eluent. Figure 5 shows the infrared spectrum of the product and Figure 6 shows the DSC thermogram of the product. The DSC shows a melting endotherm at 154° followed by an exotherm with a maximum at 220°C. We are currently (December 1982) obtaining more product for elemental analysis, hydrogenation studies and possible ^{13}C NMR examination.

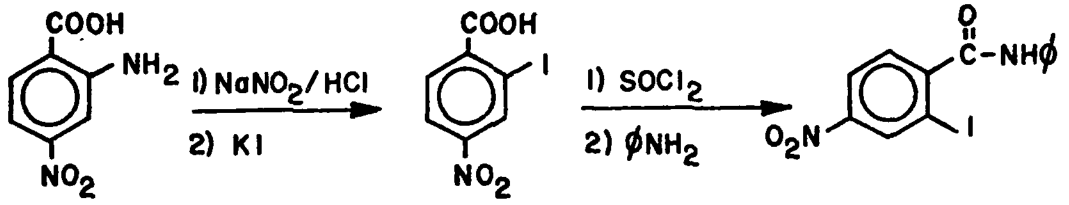
3) 2-(Phenylethynyl)-N-phenylbenzamide Functionalization

The synthesis of 2-iodo-5-nitro-N-phenylbenzamide (34) was accomplished at considerable effort. The literature[22] concerning the nitration of o-iodobenzoic acid (32) is vague if not incorrect as to the location of the product during purification and separation of 5-nitro-2-iodobenzoic acid (33a) from 3-nitro-2-iodobenzoic acid, (33b)a by product. The reaction of 33a with thionyl chloride followe[illegible] reaction of the acid chloride with aniline provided 34 in excellent yield.



32 33a,b 34

The synthesis of 2-iodo-4-nitro-N-phenylbenzamide (37) also required considerable effort. The conversion of 4-nitroanthranilic acid (35) to 2-iodo-4-nitrobenzoic acid (36) was best accomplished by a procedure reported by Baker, et. al.[23] in preference to an earlier reported procedure.[24] The amidation of 36 as earlier described, yielded 37 in excellent yield.



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IV. Contract Personnel

The research effort described herein was conducted in part by Stefan Alan Babirad. Stefan received his Master's Degree in Chemistry from Wright State University in August 1982 (thesis unrelated to contract). He is now a graduate student at Carnegie-Mellon University pursuing a Ph.D. degree in Polymer Chemistry.

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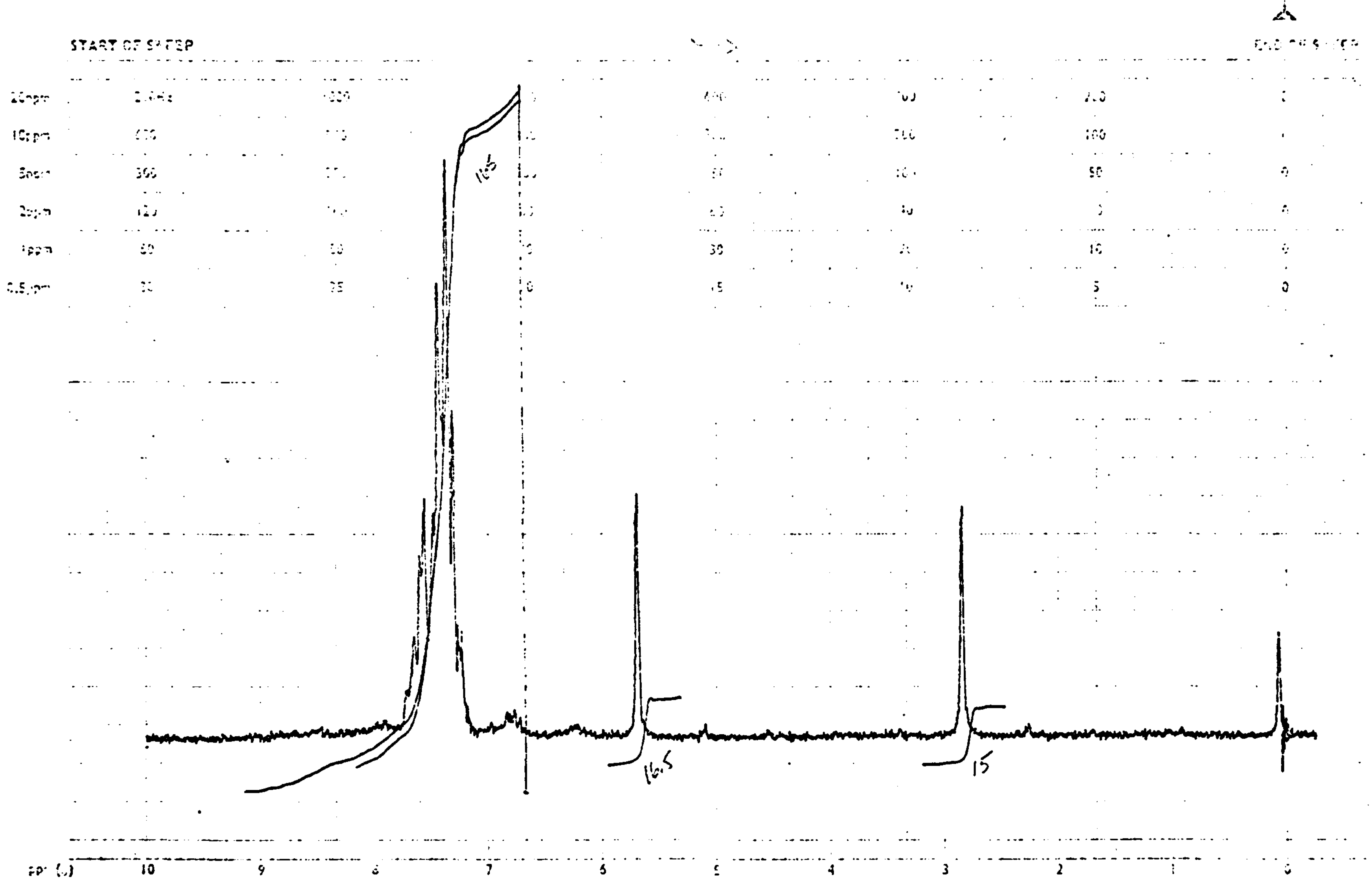

Figure 1. The NMR spectrum of 1,3-diphenyl-2-propyn-1-ol (31).

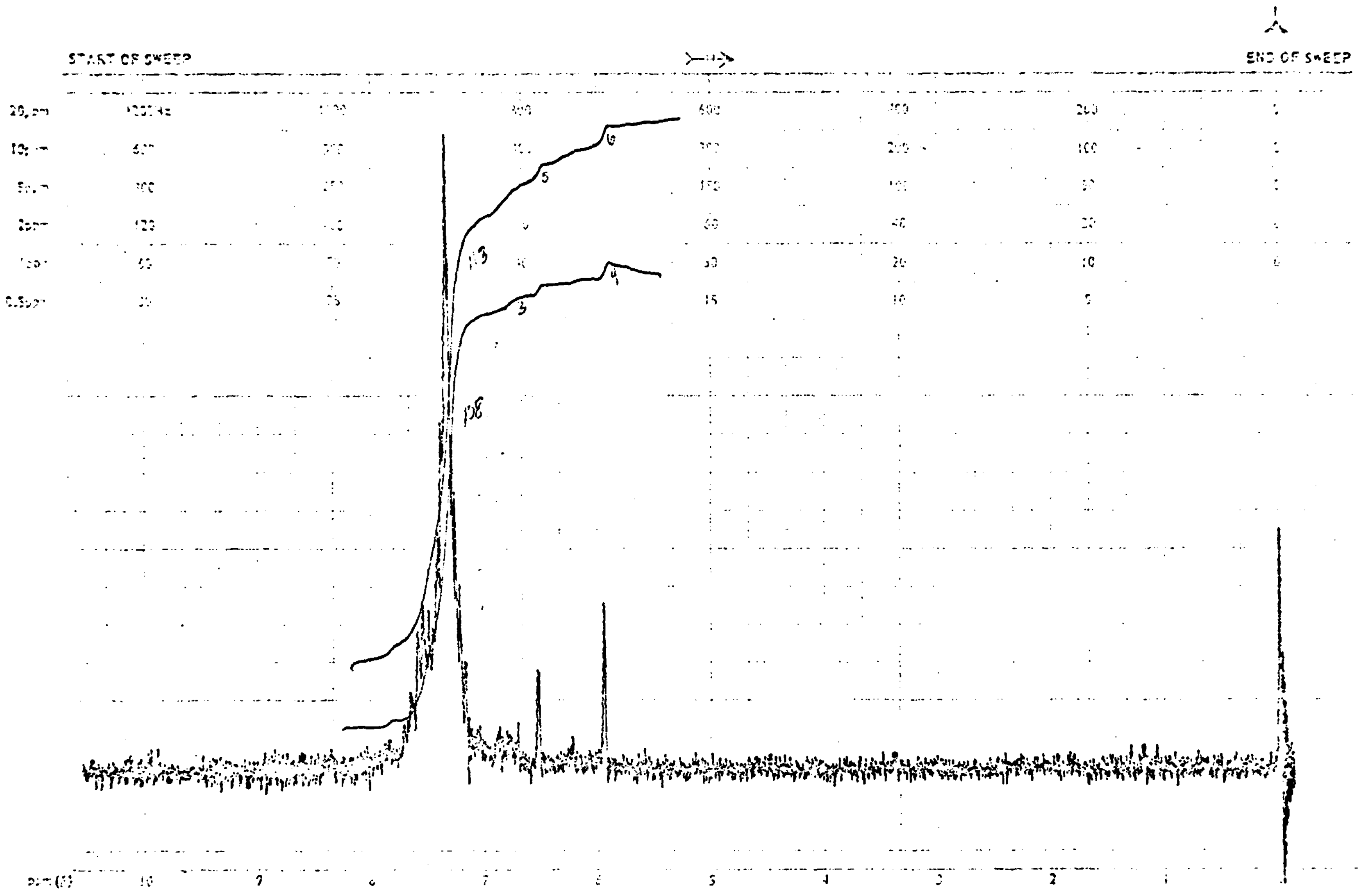

Figure 2. The NMR spectrum of 3-bromo-1,3-diphenylpropyne (29).

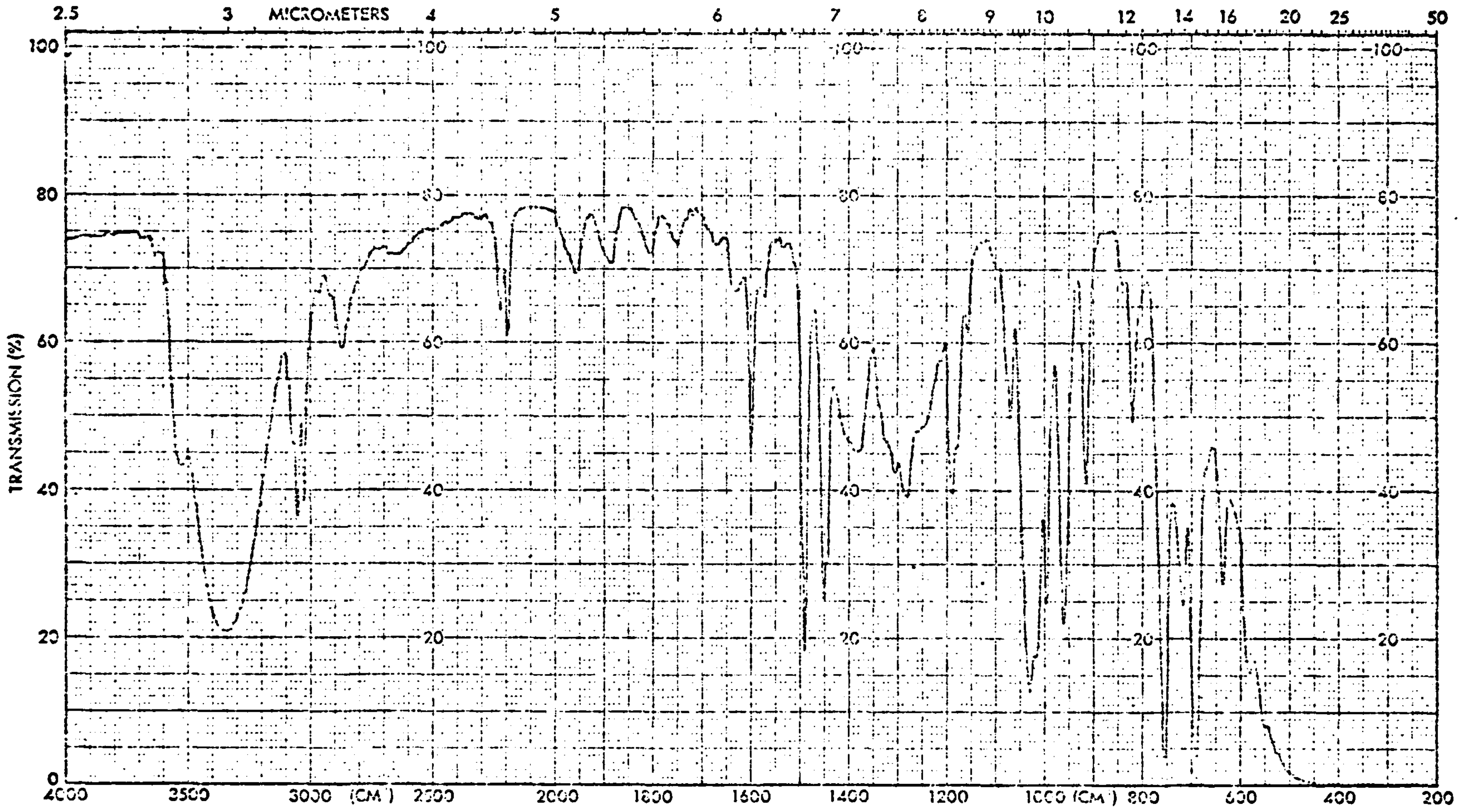

Figure 3. The IR spectrum of 1,3-diphenyl-2-propyn-1-ol (31).

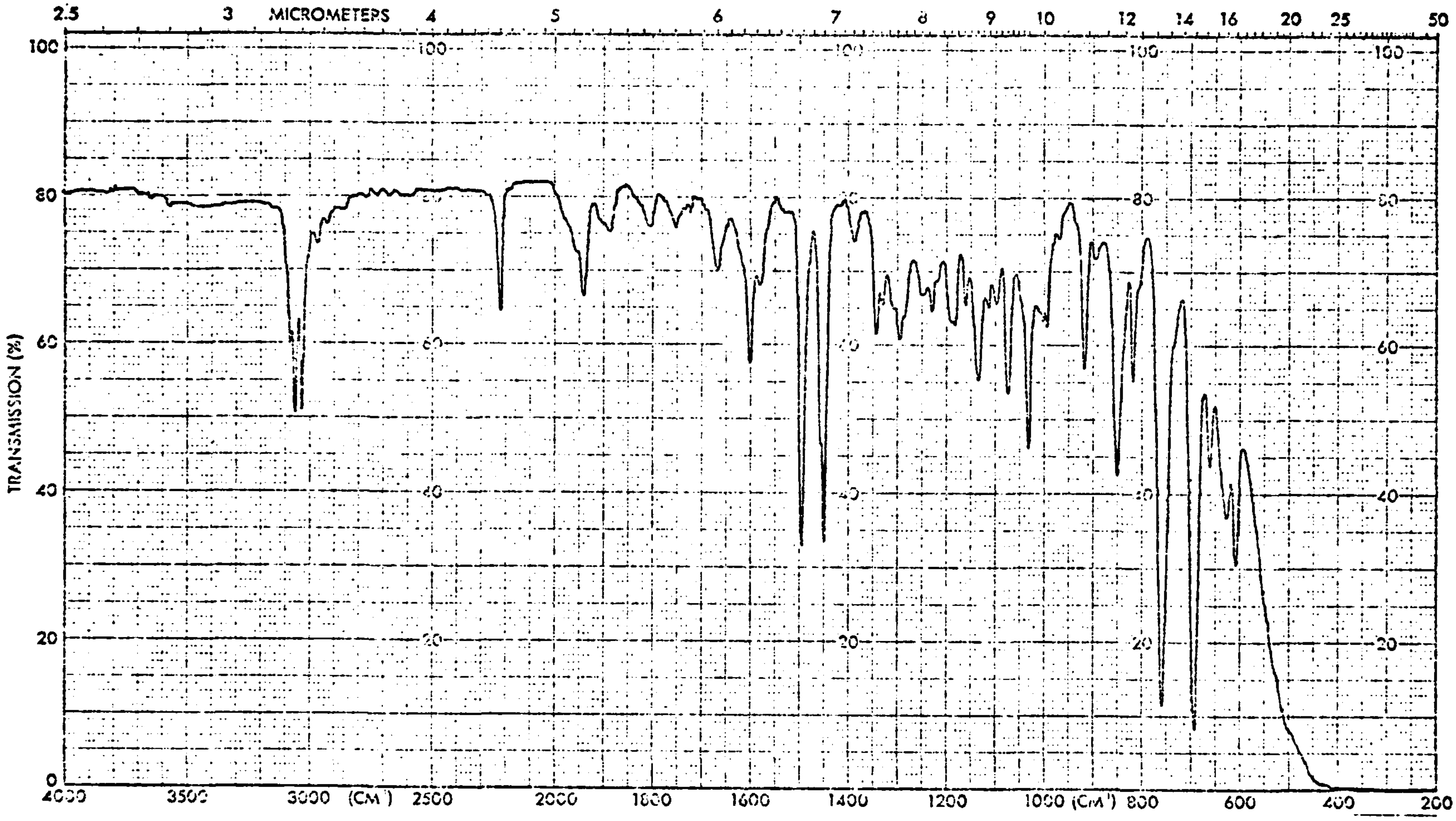

Figure 4. The IR spectrum of 3-bromo-1,3-diphenylpropyne (29).

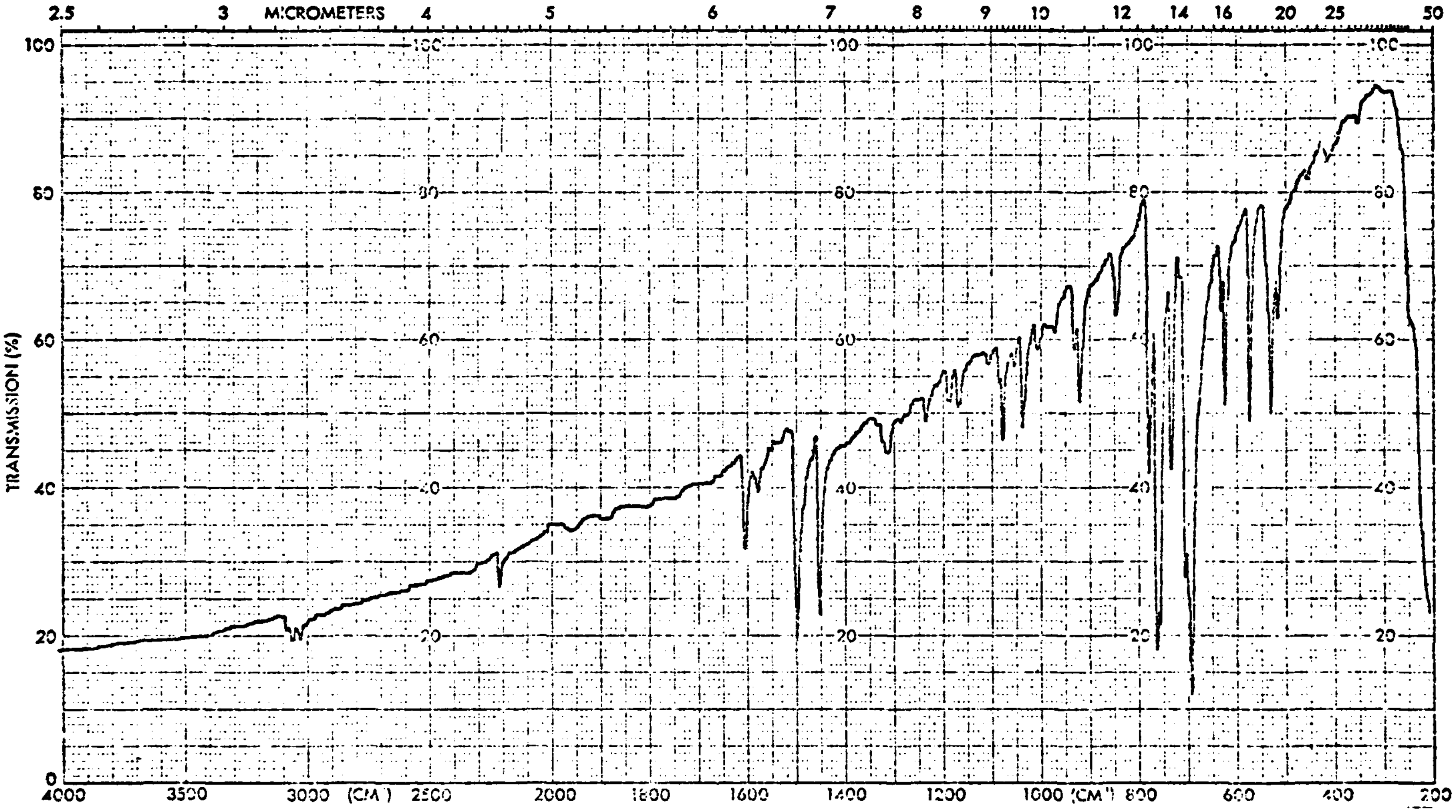

Figure 5. The IR spectrum of 1,3,4,6-tetraphenylhexa-3-ene-1,5-diyne (21).

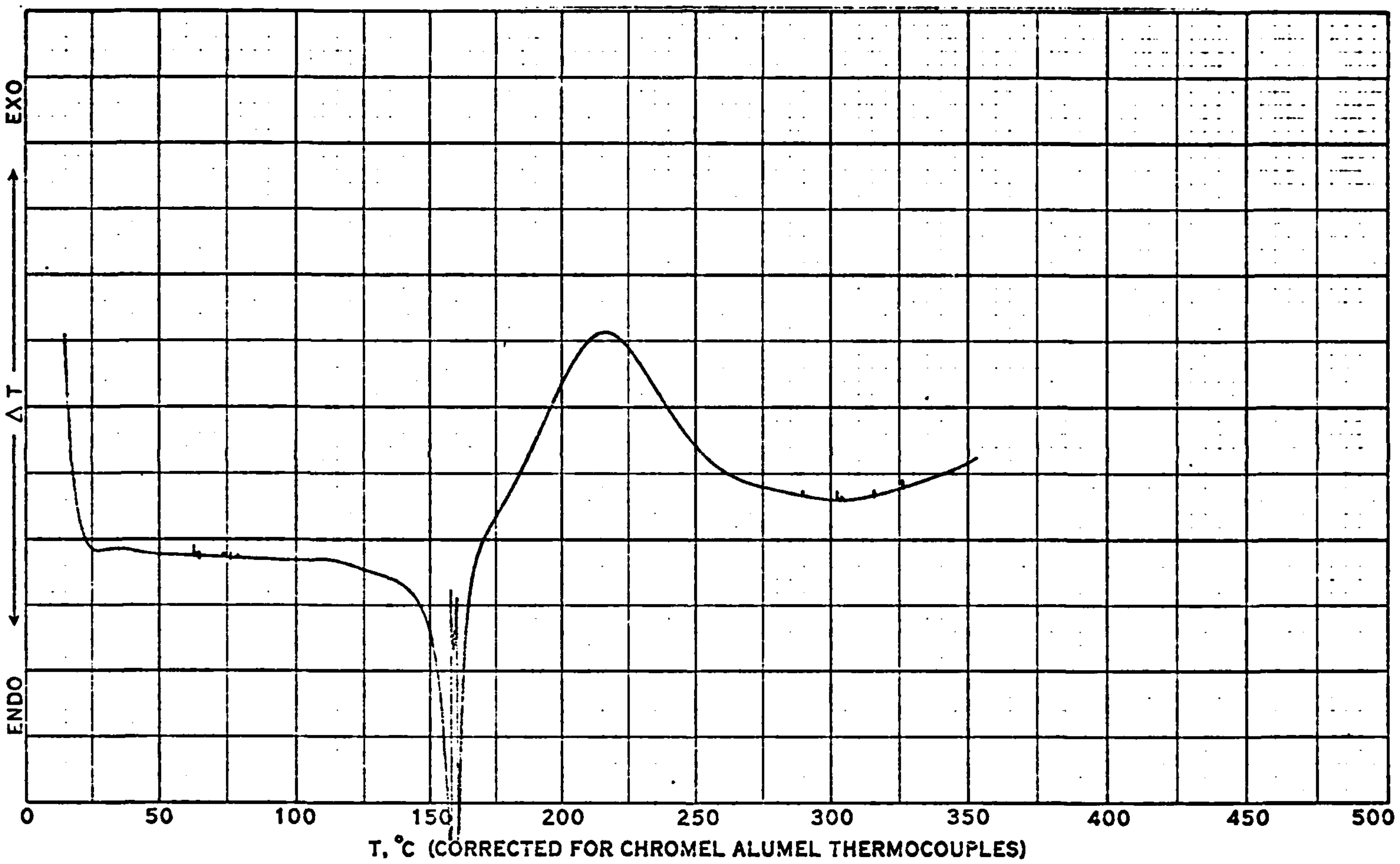

Figure 6. The Differential Scanning Calorimetric (DSC) determination for 1,3,4,6-tetraphenylhexa-3-ene-1,5-diyne (21).