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4-(4-Ethynylphenoxy)benzil was separately reacted with two amidrazones to provide acetylene-containing phenyl-*as*-triazine products. Each product consisted of two isomers which were separated by high pressure liquid chromatography and analyzed by mass spectroscopy. Differential scanning calorimetry was employed to study the thermal reaction of the acetylene-containing phenyl-*as*-triazine products. The principal component from the thermally induced reaction of the acetylene-containing phenyl-*as*-triazine was identified by mass spectroscopy as a dimer.

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As part of a high temperature structural resin program, work is being directed towards the preparation and thermal chain extension of acetylene-terminated heterocyclic oligomers. Our initial work involved the phenylquinoxaline system (3) and particularly the synthesis and thermal reaction of an acetylene-containing phenylquinoxaline compound (4). This work has now been extended to the phenyl-*as*-triazine system. Acetylene-containing phenyl-*as*-triazine compounds were prepared, characterized and their thermally induced reaction studied. This work was performed to obtain information regarding reaction conditions required for the polymer chain extending reaction and to identify the major component resulting from the thermal reaction of the ethynyl group.

4-(4-Ethynylphenoxy)benzil was prepared as previously reported (4) by treating 4-(4-acetylphenoxy)benzil with excess Vilsmeier reagent (a 1:1 complex of phosphorus oxychloride and *N,N*-dimethylformamide) to yield 4-(4-phenylglyoxalylphenoxy)- β -chlorocinnamaldehyde which was subsequently cleaved with aqueous sodium hydroxide. The yield of 4-(4-ethynylphenoxy)benzil from that previously reported (4) was significantly improved (72% versus 20%) by adding an aqueous sodium hydroxide solution to a dioxane solution of the β -chlorocinnamaldehyde and maintaining the temperature < 299° K (26°). Higher temperatures with excess sodium hydroxide as used in the previously reported synthesis (4) resulted in excessive cleavage of the α -diketone. 4-(4-Ethynylphenoxy)benzil was obtained as a yellow oil in spite of various attempts to induce crystallization by trituration and cooling. This was surprising since 4-(3-ethynylphenoxy)benzil was reported to be a pale yellow solid melting at 352-354° K (79-81°) (5).

Perfluorobutyramidrazone was prepared by bubbling perfluorobutyronitrile into a solution of hydrazine in isopropanol at 270° K (5°). After complete addition, the solution was stirred at ambient temperature for 2 hours followed by removing the isopropanol under vacuum at < 303° K (30°); The resulting white crystalline solid was washed with cold isopropanol and recrystallized from

cyclohexane to yield white platelets of perfluorobutyramidrazone.

2-Pyridylamidrazone was prepared from the reaction of 2-cyanopyridine and hydrazine in ethanol. Near white needles of 2-pyridylamidrazone were obtained after recrystallization of the yellow product from benzene.

The reaction of 4-(4-ethynylphenoxy)benzil with perfluorobutyramidrazone and 2-pyridylamidrazone in ethanol is shown in Equation 1. The product from each reaction melted over a 7° K range while the elemental analysis agreed well with the theoretical values as shown in Table 1. High pressure liquid chromatography (HPLC) disclosed two components in each product with the relative amounts indicated in Equation 1. The presence of two components in each product was expected due to the anticipated difference in the reactivity of the two carbonyl groups. The carbonyl adjacent to the phenyl group

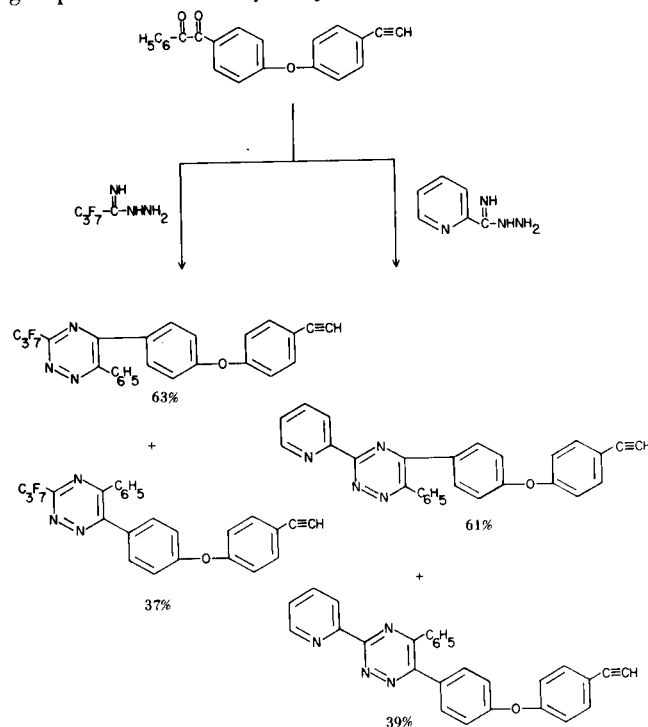
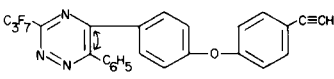
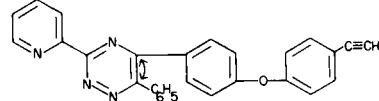


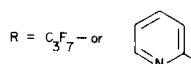
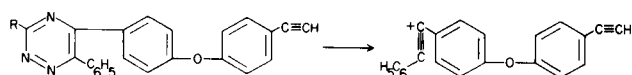
Table 1
Characterization of Model Compounds

Compound		
Form	Yellow Glass	Yellow Solid
M.p.° K (°C)	318-325 (45-52)	336-343 (63-70)
Formula	C ₂₆ H ₁₄ F ₇ N ₃ O	C ₂₈ H ₁₈ N ₄ O
Mol. Wt. (a) (Theoretical)	517 (517)	426 (426)
Elemental Analysis (Theoretical)	% C 59.98 (60.36) % H 2.77 (2.72) % N 8.36 (8.12) % F 25.42 (25.70)	% C 78.86 (78.86) % H 4.29 (4.25) % N 13.13 (13.14)

(a) Determined by Mass Spectroscopy.

should be the more reactive since the electron density of the other carbonyl would be expected to be higher from contribution of electrons from the ether oxygen. The terminal nitrogen on the hydrazino portion of the amidrazone would be expected to attack this carbonyl preferentially, thus providing the compound with the phenyl group located in the 6-position as the predominant isomer.

A preparative separation by HPLC of each product was performed (Figure 1) and the two isomers from each product were analyzed by mass spectroscopy. The electron-impact fragmentation pattern was essentially identical for each of the two isomers from each product as shown in Figures 2 and 3. The principal fragment from each isomer had an *m/e* of 294 which corresponded with the cleavage of the *as*-triazine ring as depicted in Equation 2. The molecular ions are not present in the spectra in Figure 3 due to the small amounts of sample used to obtain the spectra. The structure of each isomer was assigned to each mass spectrum based on the liquid chromatographic separation and knowing which isomer should predominate.



The thermal reaction of an acetylene group on a heterocyclic parent compound is complex as shown in previous work with acetylene-containing phenylquin-

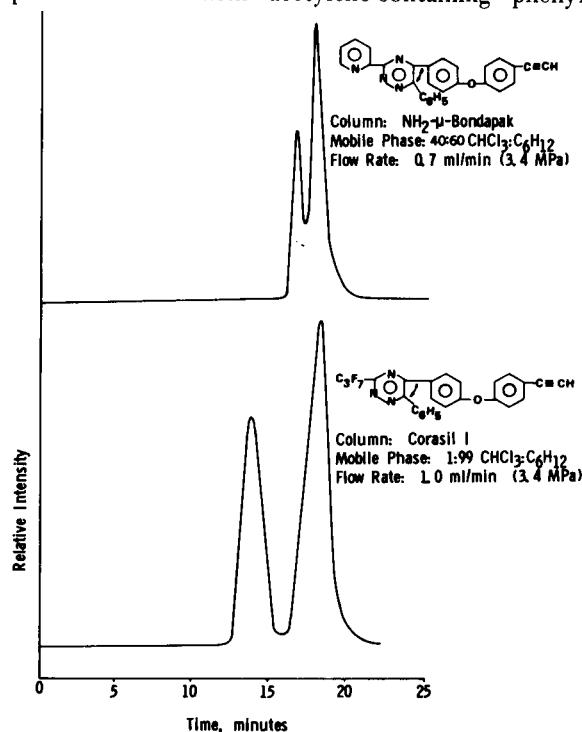


Figure 1.-High Pressure Liquid Chromatograms of Products

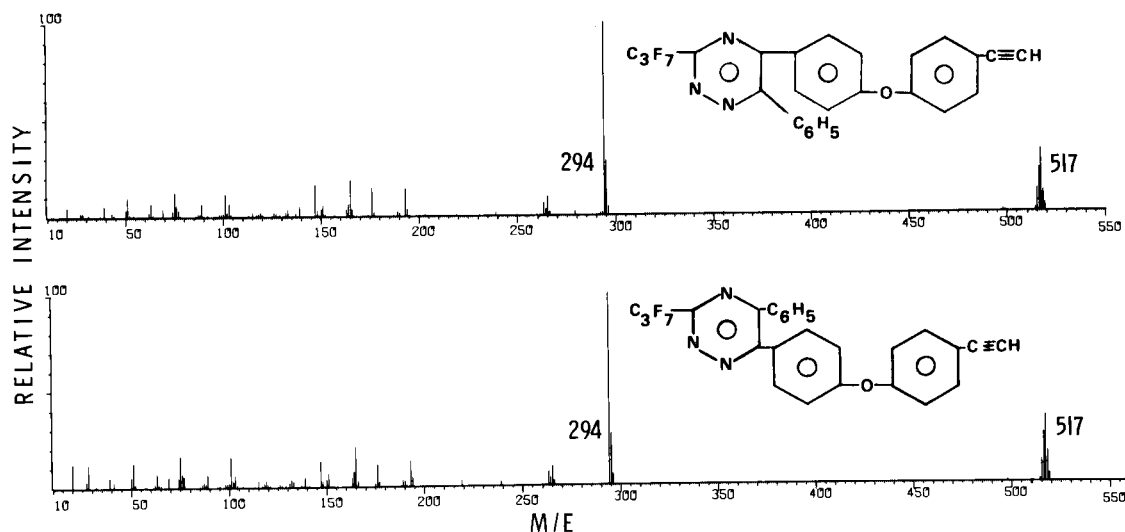


Figure 2.- Mass Spectra of Perfluoropropyl Isomers.

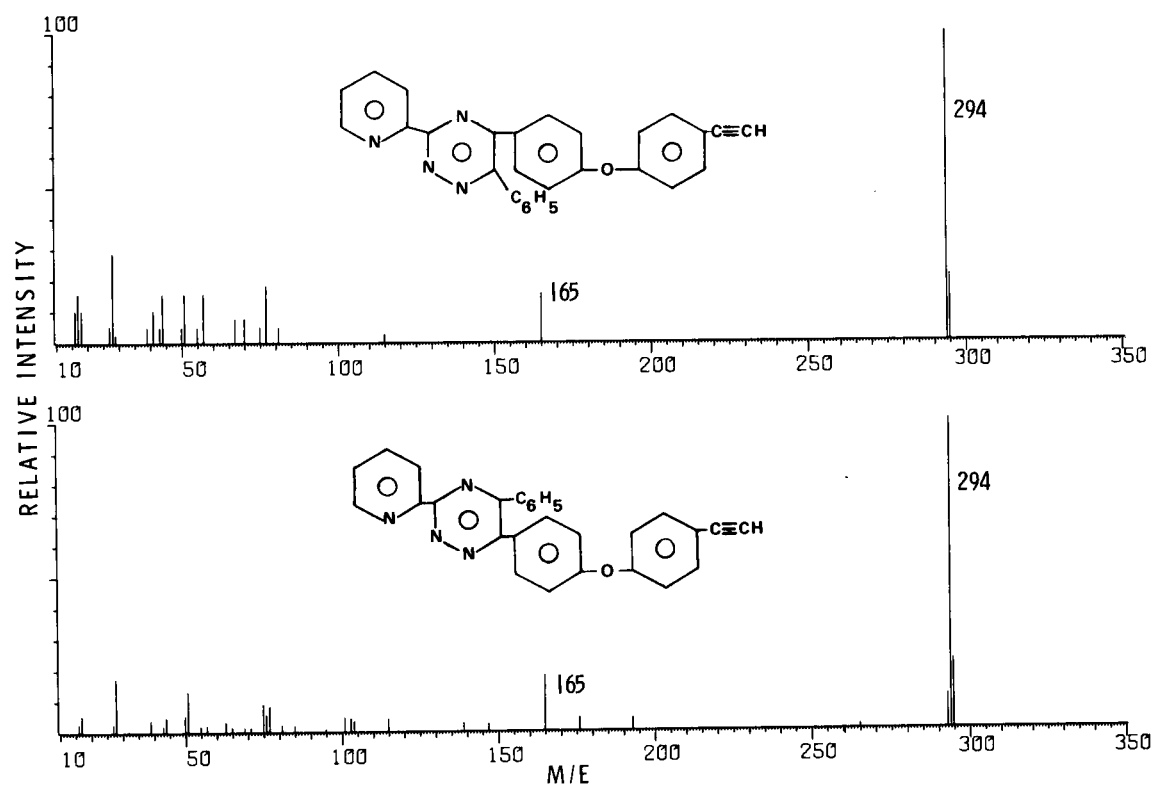


Figure 3.- Mass Spectra of 2-Pyridyl Isomers.

oxalines (4,6). The reaction is even more complex when a mixture of two isomers is thermally reacted. The acetylene group can yield a variety of products from a thermal reaction. Dimers as well as several other species such as benzene and cyclooctatetrene derivatives may be

formed. Of the two possible stable dimers ($-C\equiv C-CH=CH-$ and $-C\equiv C-\overset{CH_2}{\underset{|}{C}}-$), the vinylidene type would be favored by an ionic mechanism. A vinylidene compound appeared to be the major component in a 623° K (350°) reaction

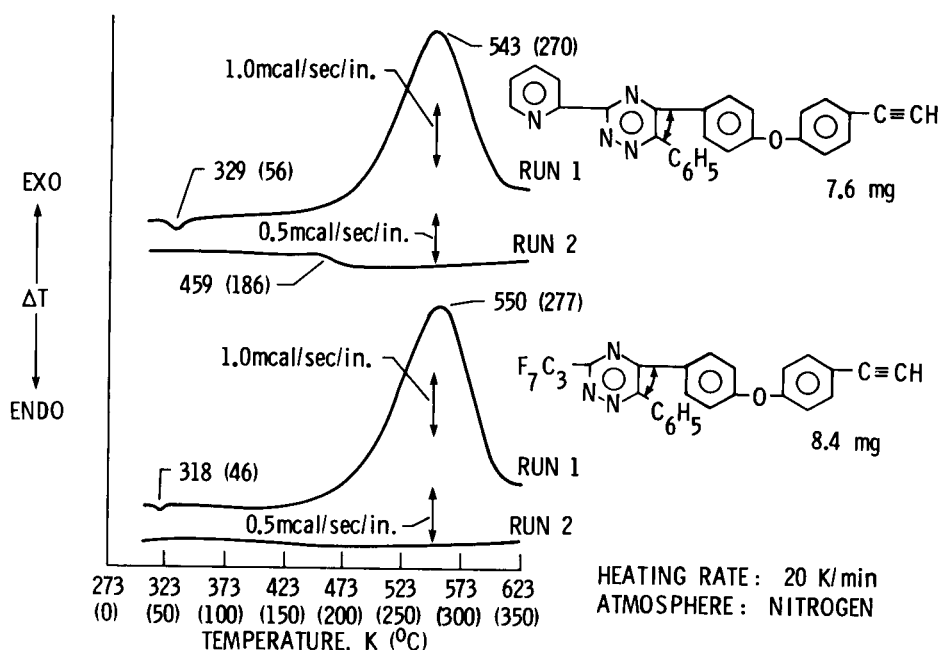


Figure 4. - Differential Scanning Calorimetry Curves of Acetylene-Terminated Phenyl-*as*-triazine Compounds.

product of an acetylene-containing phenylquinoxaline (4).

The differential scanning calorimetry (DSC) curves from 299° K (26°) to 623° K (350°) for the two acetylene-containing phenyl-*as*-triazine products are shown in Figure 4. The perfluoropropyl and 2-pyridyl products gave similar DSC curves with melting endotherms peaking at 319° K (46°) and 329° K (56°) and broad exotherms from 423° K (325°) peaking at 550° K (277°) and 543° K (270°), respectively. Upon rerunning each sample after heating to 623° K (350°) in nitrogen, the 2-pyridyl sample gave a baseline deflection at 459° K (189°) characteristic of a second order transition whereas no major thermal transitions were detected for the perfluoropropyl sample. The infrared spectra of each acetylene-containing phenyl-*as*-triazine product showed a C≡C-H stretch at 3.02 μ and C≡C at 4.7 μ which disappeared upon heating to 623° K (350°) in nitrogen indicating the strong exotherm in the DSC curve was due to reaction of the ethynyl group.

The heat of reaction (ΔH) was determined at a heating rate of 5, 10, 20 and 50° K per minute for each product using tin as a standard. The heat of reaction was found to be independent of heating rate indicating that the thermal reaction proceeded faster than the fastest heating rate. The perfluoropropyl and pyridyl products gave ΔH of 40.7 ± 1 and 41.4 ± 1 cal/mole, respectively, under each of the 4 heating rates. The ΔH for the two compounds was expected to be essentially the same due to their similarity. The ethynyl portion of the two products is the same and its reaction should not be influenced by

the other end of the molecule except perhaps for molecular mobility.

It was of interest to know the minimum temperature to initiate the reaction of the acetylene group, the effect of higher temperature upon the product, and the identity of the major component in the product. Samples of the two acetylene-containing phenyl-*as*-triazine products were individually heated for 0.5 hour at 468° K (195°), 522° K (250°), 568° K (295°), and 623° K (350°) in nitrogen and each soluble product analyzed by HPLC. The products after heating the perfluoropropyl samples at each of the 4 temperatures were soluble in chloroform and were analyzed by HPLC. The chromatogram of the 468° K (195°) sample show that 55.9% of the perfluoropropyl model compound remained unchanged while the remaining 44.1% consisted of two peaks. These quantities were determined by measuring the areas under the peaks. After 0.5 hour at 523° K (250°), only 9.0% of the perfluoropropyl material remained unchanged with the remainder represented by several peaks. After 0.5 hour at 568° K (295°) and 623° K (350°), no unreacted perfluoropropyl material was detected in the reaction product. Separation of the reaction product into moderately well-resolved peaks was unsuccessful even though various columns, solvent combinations, and detectors were used in the normal and reverse phase modes. No single major component could be resolved.

The 568° K (295°) products of the perfluoropropyl and 2-pyridyl compounds were analyzed by mass spectroscopy. The spectra shown in Figures 5 and 6 were

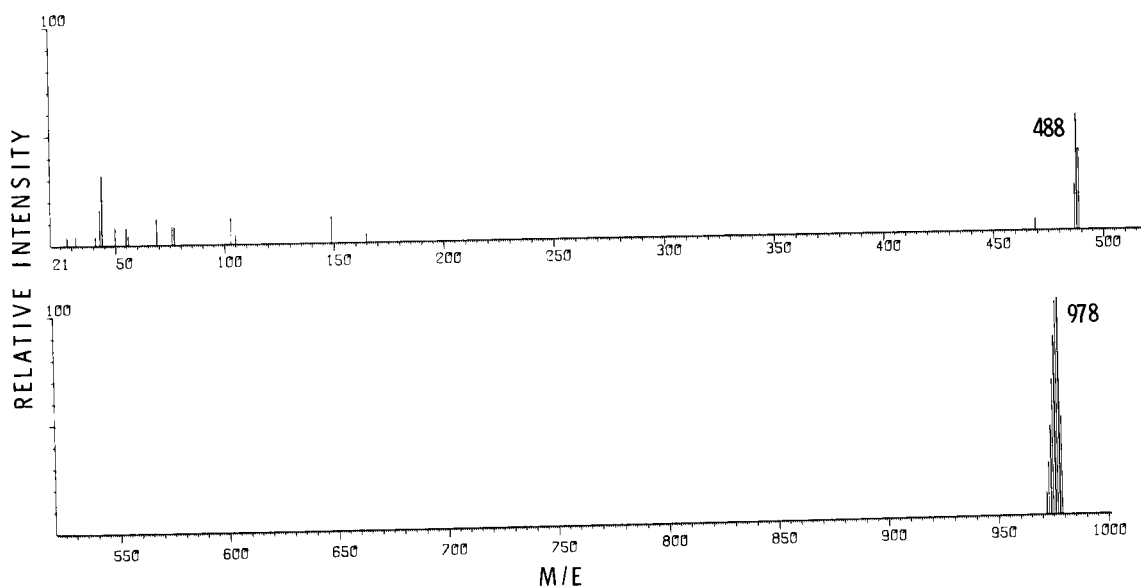


Figure 5.- Mass Spectra of 568K (295°C) Product of Perfluoropropyl Compounds.

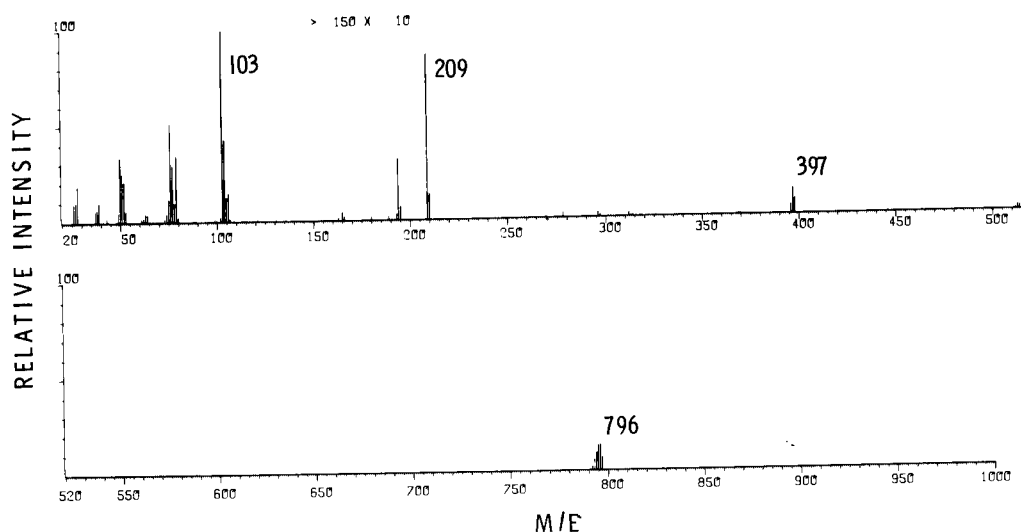


Figure 6.- Mass Spectra of 568K (295°C) Product of 2-Pyridyl Compounds.

exceptionally clean. This was surprising since the parent phenyl-*as*-triazine compounds contain isomers and therefore were expected to provide complex fragmentation patterns. As shown in Equation 3, the thermal reaction of an acetylene-containing phenyl-*as*-triazine compound yielded a dimer as evidence from its electron impact fragmentation pattern. The mass spectra from each of the 568° K (295°) exposed samples gave a high molecular weight fragment whose m/e corresponded with the loss of 56 (four nitrogen atoms) from the dimer. This fragmentation route is surprisingly different from that of the starting material as depicted in Equation 2 and shown in Figures 2 and 3. No explanation is offered to account for this

difference.

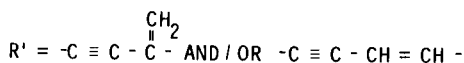
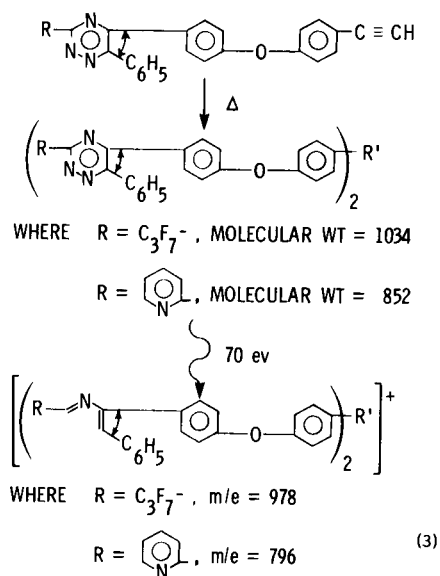
The 568° K (295°) product from each compound was examined by infrared spectroscopy in an attempt to

determine which dimer ($-C\equiv C-C-$ or $-C\equiv C-CH=CH-$) had formed. The infrared spectra were complex which prohibited a definite conclusion as to the structure of the dimer. However, the presence of a dimer from the mass spectroscopy work as the major component in the thermally reacted product agreed with the findings from the acetylene-containing phenylquinoxaline work (1).

EXPERIMENTAL

All melting points are uncorrected. High pressure liquid chromatography was performed with a Waters Associates Model ALC 202/R401 instrument with a Model 6000 Solvent Delivery System using the indicated column and a 254 nm fixed wavelength ultraviolet detector. A Dupont Model 990 Thermal Analyzer in combination with a standard DSC cell (Dupont Catalog No. 900600-902) was used for all calorimetry measurements. The samples were hermetically sealed in Dupont supplied aluminum cups. Each sample was weighed before and after each DSC run. Essentially no change in weight was observed. The ΔH was determined by running the DSC on the time base mode at four different heating rates. The area of the transition peak was determined by drawing a line from the point where the thermogram departed from the baseline to the point where it returned. This enclosed area was measured with a planimeter.

A Finnigan Model 3300 Quadrupole Mass Spectrometer equipped with a Model 6000 Data System was used to obtain the electron-impact spectra of each compound. Samples were introduced into the ion source with a programmable temperature solid inlet probe. Each spectra was obtained by heating the sample at 2° K/minute from the ion source temperature 373° K (100°) to a temperature where enough sample was vaporized to generate a usable spectrum. Heating to 473° K (200°) was generally



sufficient. Each 70 ev spectra was obtained by repeatedly scanning the 10-1000 amu mass range over a 15 second period while the sample was heated. Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colorado.

Perfluorobutyramidrazone.

Perfluorobutyronitrile (50 g., 0.26 mole) was bubbled during 2 hours into a stirred solution of 97% hydrazine (25 ml.) in isopropanol (250 ml.) at 278° K (5°). After complete addition, the isopropanol was removed under vacuum at <303° K (30°) to provide a white precipitate which was filtered, washed with cold isopropanol, and recrystallized from cyclohexane (41 g. in 1.5 l.). Perfluorobutyramidrazone was obtained as white platelets (35 g., 59% yield), m.p. 341.5-342.5° K (68.5-69.5°)

[lit. m.p. 342-343° K (69.5-70°) (7)].

2-Pyridyl Amidrazone.

2-Cyanopyridine was reacted with hydrazine in ethanol according to a known procedure (8) to yield a pale yellow solid. Recrystallization from benzene afforded 2-pyridyl amidrazone as near white needles, m.p. 367-368° K (94-95°) [lit. m.p. 369-369° K (95-96°) (8)].

4-(4-Ethynylphenoxy)benzil.

This compound was prepared by a modification of a known procedure (4). This involved the addition of an aqueous sodium hydroxide solution to the β -chlorocinnamaldehyde in dioxane rather than the reverse addition previously used. A solution of sodium hydroxide (3.0 g., 75 mmoles) in water (50 ml.) was added dropwise during 0.5 hour to a stirred solution of 4-phenylglyoxalylphenoxy- β -chlorocinnamaldehyde (3.0 g., 7.7 mmoles) in dioxane (50 ml.) at 288° K (15°). After complete addition, the brown reaction mixture was stirred at 299° K (26°) for 2 hours followed by pouring it into cold water (300 ml.). The orange aqueous solution was allowed to stand for 4 hours and decanted to leave a residual gum. The gum was dissolved in methylene chloride (100 ml.), and the solution was washed three times with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The residual yellow gum was dissolved in hot cyclohexane (200 ml.) and the solution was treated with charcoal, filtered, and concentrated to yield 4-(4-ethynylphenoxy)benzil (1.8 g., 72% yield) as a yellow gum.

Anal. Calcd. for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 80.83; H, 4.29.

2-Heptafluoropropyl-5-phenyl-6-[4-(4-ethynylphenoxy)phenyl]-*as*-triazine (and isomer).

A solution of 4-(4-ethynylphenoxy)benzil (0.9700 g., 3.0 mmoles) and perfluorobutyramidrazone (0.6813 g., 3.0 mmoles) in ethanol (20 ml.) was stirred at ambient temperature for 3 days and at the reflux temperature for 3 hours. The orange solution was concentrated to dryness to provide a residual orange gum which slowly solidified. The glassy orange solid was dissolved in cyclohexane (20 ml.) and the solution was treated with charcoal and filtered. The cooled filtrate was concentrated to dryness to provide 2-heptafluoropropyl-5-phenyl-6-[4-(4-ethynylphenoxy)phenyl]-*as*-triazine (and isomer) as a glassy yellow solid (1.3 g., 87% yield). Characterization is given in Table 1.

2-(2-Pyridyl)-5-phenyl-6-[4-(4-ethynylphenoxy)phenyl]-*as*-triazine (and isomer).

A solution of 4-(4-ethynylphenoxy)benzil (1.6316 g., 5.0 mmoles) and 2-pyridylamidrazone (0.6810 g., 5.0 mmoles) in ethanol (80 ml.) was stirred at ambient temperature for 0.5 hour and at the reflux temperature for 0.5 hour. The hot orange solution was treated with charcoal, filtered, and the filtrate concentrated to dryness to yield an orange gum. The orange gum was dissolved in benzene (50 ml.), and the solution was treated with charcoal, filtered, and concentrated to dryness to afford 2-(2-pyridyl)-5-phenyl-6-[4-(4-ethynylphenoxy)phenyl]-*as*-triazine (and isomer) as a yellow solid (1.9 g., 85% yield). The yellow solid was dissolved in cyclohexane (150 ml.), and the solution was treated with charcoal, and filtered. The cooled filtrate was concentrated to dryness to yield 2-(2-pyridyl)-5-phenyl-6-[4-(4-ethynylphenoxy)phenyl]-*as*-triazine (and isomer) as a yellow solid. Characterization is given in Table 1.

Thermal Reaction of the Model Compounds.

Small portions (~20 mg.) of the acetylene-containing phenyl-*as*-triazine products were heated in the DSC cell at a rate of 20°

K/minute in a nitrogen atmosphere and held for 0.5 hour at 468° K (195°), 523° K (250°), 568° K (295°), and 623° K (350°). Each sample was analyzed by HPLC and mass spectroscopy. Problems were encountered in obtaining well-resolved chromatograms for the soluble samples exposed to temperatures of 523° K (250°) and higher even though various columns, solvents, and detectors were used in the normal and reverse phase modes.

REFERENCES AND NOTES

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