chloroform; then the washings were combined and evaporated to dryness leaving a pale yellow oil (86 mg, 0.83 mmole). The infrared spectrum of this material was completely superimposable upon that of an authentic sample of 2-cyanopyridine.

The solid residue (63 mg), which was neither soluble in hexane, chloroform, nor water, did not melt below 310°. The compound was identified as cyanuric acid (**8**) by a comparison of its infrared spectrum with than of an authentic sample.[17]

2-(2-Pyridyl)-1,3,4-oxadiazole.—This compound was prepared by the method of Ainsworth.[13] Recrystallized from ethyl acetate, it had mp 117.5–118.5° (lit.[13] mp 115°); $\lambda_{max}^{CH_3OH}$ 273 mμ (log ε 3.56), 237 mμ (log ε 3.75).

3-(2-Pyridyl)-1,2,4-oxadiazole.—2-Pyridineamidoxime, mp 117.5°[18] (0.60 g, 4.4 mmoles), was treated with 5 ml of ethyl orthoformate according to the general procedure of Ainsworth.[19] The product after vacuum distillation and recrystallization from acetone–cyclohexane was obtained as white needles, mp 109–110°, yield 0.25 g (1.7 mmoles, 39%). The infrared spectrum of the product was superimposable on that of compound **4**.

5-Methyl-3-(2-pyridyl)-1,2,4-oxadiazole.—2-Pyridineamidoxime[18] (1.42 g, 10.4 mmoles) was refluxed for 10 min with 7 ml of acetic anhydride. The reaction mixture was allowed to cool and the excess acetic anhydride decomposed with ice and ammonium hydroxide. The reaction mixture was then made basic (pH 11) with 10% aqueous sodium hydroxide. This basic solution was extracted with five 50-ml portions of chloroform. The dried (anhydrous magnesium sulfate) solution was evaporated to dryness to yield a brown solid. This solid was purified by chromatography on grade III neutral alumina, to afford 1.33 g (8.3 mmoles, 79%) of 5-methyl-3-(2-pyridyl)-1,2,4-oxadiazole, mp 87–88.5°. A mixture melting point of this product with compound **5** was not depressed (mp 88–89°). The infrared spectra of these two compounds were completely superimposable, as are their nmr and mass spectra.

Registry No.—**4,** 13389-59-8; **5,** 10350-68-2; **6,** 13389-61-2; **10,** 13428-22-3.

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[17] Sadtler Infrared Spectra Catalog, Spectrum No. 12554.

[18] E. Bernasek, *J. Org. Chem.*, **22**, 1263 (1957).

[19] C. Ainsworth, W. E. Bunting, J. Davenport, M. E. Callender, and M. C. McCowen, *J. Med. Chem.*, **10**, 208 (1967).

Pyrolysis of Aromatic Azines[1]

STEPHEN S. HIRSCH

Chemstrand Research Center, Inc., Durham, North Carolina

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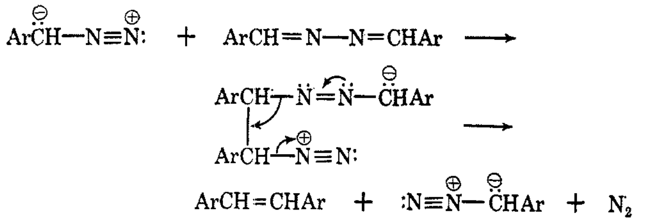
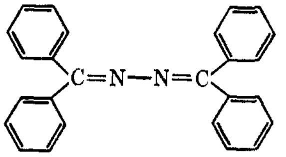
The pyrolysis of benzal azine to stilbene and nitrogen *via* an aryldiazomethane mechanism has been reported. The observation that benzophenone azine gave no tetraphenylethylene and only a trace of nitrogen prompted an investigation of the differences between aldazine and ketazine pyrolysis mechanisms. Benzophenone azine decomposes by a free-radical process at 375–500° to afford principally benzhydrylidenimine, benzonitrile, and 6-phenylphenanthridine accompanied by lesser quantities of benzene, biphenyl, diphenylmethane, and benzhydrylideneaniline. Details of the mechanism proposed will be discussed. Failure of the aryldiazomethane moiety to participate is attributed to steric effects. The large quantity of benzhydrylidenimine formed is noteworthy, as the only source of hydrogen present is aromatic. Because aldazines and the ketazine pyrolyze so differently, the "mixed" azine, benzhydrylidene-benzylidene azine, was investigated. Identification of the pyrolysis products revealed that both the molecular and free-radical mechanisms were participating. Analysis of the data showed that in this case the aryldiazomethane mechanism proceeds *via* diphenyldiazomethane rather than phenyldiazomethane.

Few references to the pyrolysis of azines have appeared in the literature. While an earlier study by Howard, *et al.*,[2] was incomplete, the more recent work by Zimmerman and Somasekhara[3] dealing with aldazine pyrolysis was definitive. The latter workers demonstrated that aldazines decompose thermally by the following mechanism which involves participation of an aryldiazomethane intermediate. Nitrogen is not merely "split out". It was expected, then, that tetraphenylethylene would be observed as a major product from the pyrolysis of benzophenone azine (II) in analogy to the formation of stilbene from benzal azine. Examination of the gas chromatogram of the benzophenone azine pyrolysate from an experiment conducted at 476° (Figure 1) failed to show the presence of any significant quantity of tetraphenylethylene, while only a trace peak attributable to nitrogen was observed. Clearly, reaction was not occurring according to the scheme advocated for aldazine pyrolysis.





II

The major products of the flash pyrolysis of benzophenone azine over the temperature range 375–500° are benzhydrylidenimine (III), benzonitrile (IV), and 6-phenylphenanthridine (V), together with lesser quantities of benzene and benzhydrylideneaniline and traces of biphenyl, diphenylmethane, and nitrogen. Identification of these products was made by gas

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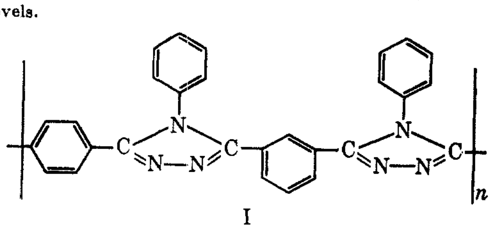
[1] Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966. This work was undertaken as part of a study to determine the reason for failure of fibers and films of poly-3,5-(*m*,*p*-phenylene)-4-phenyl-1,2,4-triazole (I) to meet expected thermostability levels.



I

[2] L. B. Howard, G. E. Hilbert, R. Wiebe, and V. L. Gaddy, *J. Am. Chem. Soc.*, **54**, 3628 (1932).

[3] H. E. Zimmerman and S. Somasekhara, *ibid.*, **82**, 5865 (1960).

Figure 1.—Gas chromatogram of the pyrolysate from the pyrolysis of benzophenone azine at 476°.

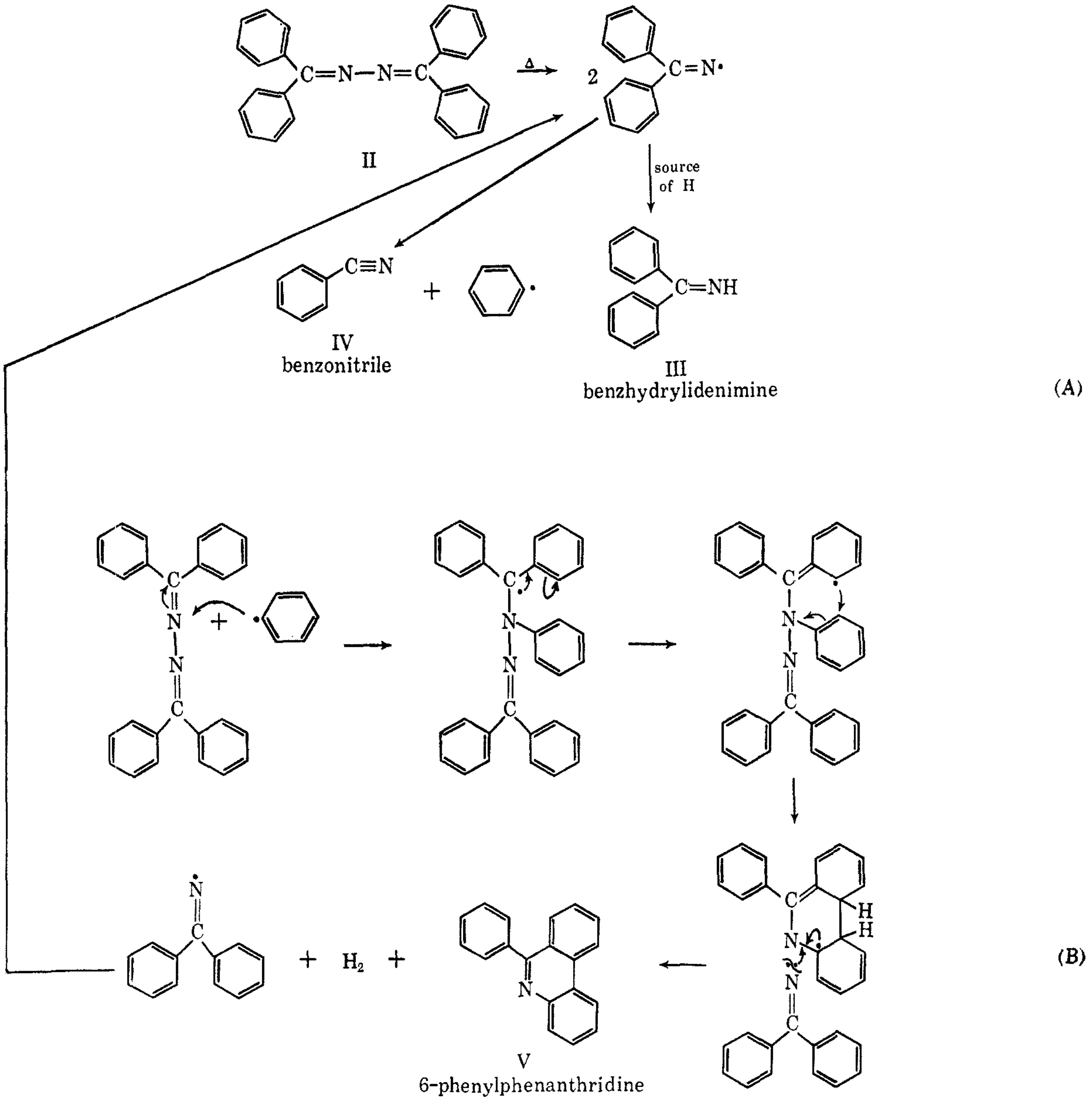
chromatography coupled with comparative infrared spectroscopy.

The reactions shown in Scheme I outline the mechanism postulated for the pyrolysis of benzophenone azine with the formation of the three major products. The dual source of benzhydrylidenimino radicals should not be overlooked; only those which do not form benzhydrylidenimine can be a source of phenyl radicals to initiate the formation of 6-phenylphenanthridine. It follows that the molar quantity of 6-phenylphenanthridine formed would not be expected to exceed that of benzonitrile. The gas chromatogram confirms this speculation. By similar reasoning, process B cannot alone be the source of benzhydrylidenimino radicals, as the sequence would cease owing to only partial formation of phenyl radicals from them. The conclusion then is that processes A and B occur together. The possibility exists that the phenyl radical attacks the nitrogen atom of the product benzhydrylidenimine, rather than (or in addition to) the benzophenone azine, to give the phenanthridine; however, this is deemed less likely. Because benzhydrylideneaniline has been observed as a minor product of the pyrolysis of benzophenone azine, it was necessary to eliminate the possibility that this anil could be converted into the phenanthridine under the conditions of the reaction. In a separate experiment, benzhydrylideneaniline was found to be an extremely thermally stable molecule and was unaffected by the temperatures required for azine pyrolysis. Temperatures sufficiently high to decompose benzhydrylideneaniline did not produce 6-phenylphenanthridine as one of the products. The formation of the minor products benzhydrylideneaniline, benzene, and biphenyl are accounted for by standard reactions of phenyl and benzhydrylidenimino radicals.

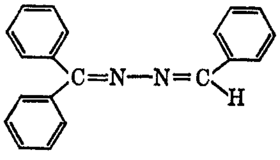
The most reasonable explanation for the failure of the aryldiazomethane mechanism to participate during the pyrolysis of benzophenone azine is on steric grounds. The bulky diphenyldiazomethane intermediate apparently cannot attack the crowded benzhydryl site. Pyrolysis is thus forced to take another course, the free-radical process described above, in which there are no steric restrictions. Benzal azine, however, doubtlessly pyrolyzes to a lesser extent by the free-radical mechanism as well, although participation of phenyl radicals must be diminished. Earlier workers[2] have reported that benzonitrile and 2,4,5-triphenylimidazole [which results *via* intermediate formation of benzalimine ($C_6H_5CH{=}NH$)] are also products of the pyrolysis of benzal azine. It is not possible to form 6-phenylphenanthridine by pyrolysis of this molecule.

The fact that the principal product of the pyrolysis is benzhydrylidenimine deserves special comment. It should be noted that this molecule contains nonaromatic hydrogen; yet only aromatic hydrogen was present in the starting material. Even under conditions as mild as flash pyrolysis at 375°, the relatively unenergetic benzhydrylidenimino radicals can secure hydrogen which must have originated from phenyl rings. In related experiments conducted with N,N,N′-triphenylbenzamidine and with poly(phenylene)triazole (I) which likewise contain aromatic hydrogen atoms only, the principal pyrolysis products (diphenylamine and aniline, respectively) also possess nonaromatic hydrogen. The presence of charred residues also reveals that hydrogen has been lost from the starting materials. Thus, it appears that aromatic hydrogen atoms can be quite labile at moderate temperatures if the over-all (in contrast to the C_6H_5–H bond strength) reaction energy changes are favorable.

Scheme I



In view of the entirely different principal courses of pyrolysis of the structurally related aldazines and the ketazine, it was of interest to determine the mode of decomposition of the half-aldazine, half-ketazine, benzhydrylidene–benzylidene azine (VI) upon thermolysis.



VI

The behavior of this "mixed" azine confirms the concepts discussed above; *both* of the described mechanisms are participating to a major extent. In Figure 2 is given the gas chromatogram of the pyrolysate resulting from thermolysis of benzhydrylidene–benzylidene azine at 495°. All products were identified by comparative infrared spectra.

Products Resulting from the Free-Radical Mechanism.—The presence in the pyrolysate of benzonitrile, benzhydrylidenimine, phenanthridine, and 6-phenylphenanthridine (as well as benzene and biphenyl) is best accounted for by participation of the free-radical mechanism described for the pyrolysis of benzophenone azine. The formation of phenanthridine or 6-phenylphenanthridine depends upon which nitrogen atom is attacked by a phenyl radical. Consideration of the possible reaction pathways reveals that the ratio of benzonitrile to any other single (free-radical) product should be greater than in the case of the ketazine. Comparison of the gas chromatograms of the pyrolysates reveals this to be the case. It should be mentioned that any benzalimine formed would be expected to be converted into 2,4,5-triphenylimidazole (lophine). Some of this compound doubtlessly is present among the higher boiling components of the pyrolysate; however, resolution of these materials by the gas chromatograph was insufficient to permit its identification.

Products Resulting from the Aryldiazomethane Intermediate.—The presence in the pyrolysate of nitrogen and triphenylethylene (and most likely the diphenylmethane and fluorene[4]) is best accounted for by partici-

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[4] A divalent carbon intermediate is probably a contributing species.

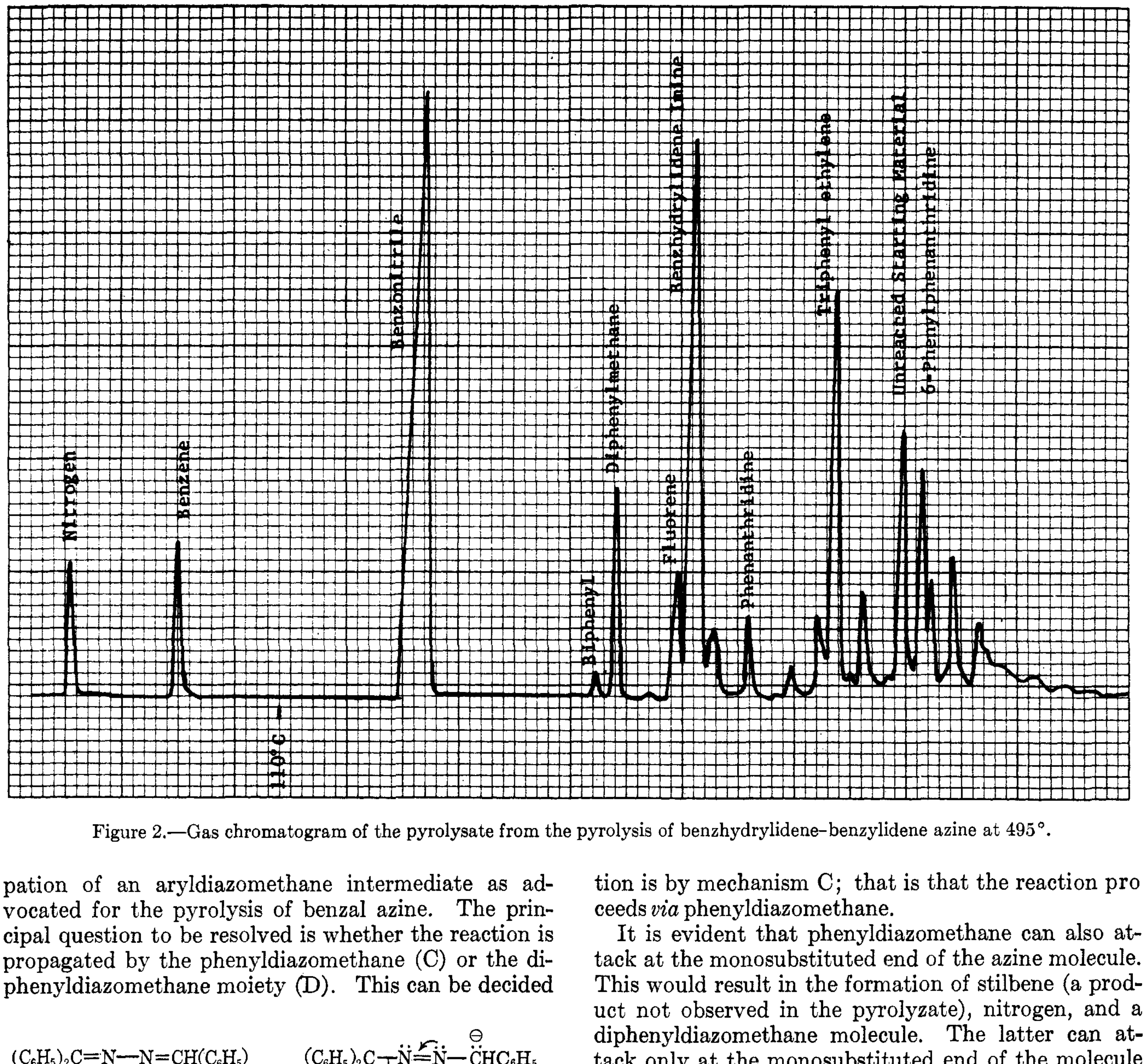
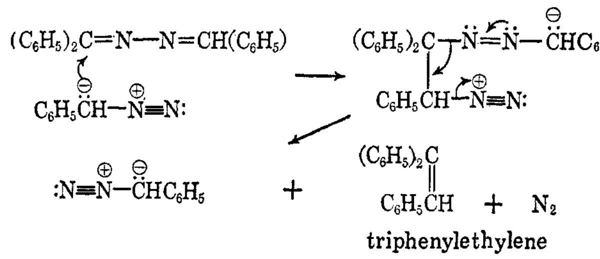
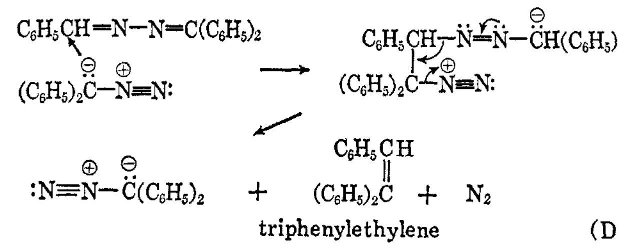


Figure 2.—Gas chromatogram of the pyrolysate from the pyrolysis of benzhydrylidene-benzylidene azine at 495°.

pation of an aryldiazomethane intermediate as advocated for the pyrolysis of benzal azine. The principal question to be resolved is whether the reaction is propagated by the phenyldiazomethane (C) or the diphenyldiazomethane moiety (D). This can be decided



(C)



(D)

by taking into account the fact that the diphenyldiazomethane molecule *cannot* attack the disubstituted end of the mixed azine, as was learned from the pyrolysis of benzophenone azine and from the fact that no tetraphenylethylene is observed in the pyrolysate from the mixed azine. Let us assume that propagation is by mechanism C; that is that the reaction proceeds *via* phenyldiazomethane.

It is evident that phenyldiazomethane can also attack at the monosubstituted end of the azine molecule. This would result in the formation of stilbene (a product not observed in the pyrolyzate), nitrogen, and a diphenyldiazomethane molecule. The latter can attack only at the monosubstituted end of the molecule as described in mechanism D. Thus, any attempt of the reaction to proceed *via* mechanism C would be forced immediately to revert to formulation D. The conclusion is, therefore, that that portion of the pyrolysis of benzhydrylidene benzylidene azine which proceeds *via* an aryldiazomethane moiety does so overwhelmingly by mechanism D, that is through diphenyldiazomethane. This is also consistent with the observation of diphenylmethane and fluorene, but not a trace of toluene, in the pyrolysate. Note also that far less diphenylmethane is present in the pyrolysate from benzophenone azine.

Experimental Section

Apparatus and Method.—The apparatus used in this study consisted of a modified Perkin-Elmer pyrolysis accessory unit used in series with an F & M Model 500 dual column, temperature programmed gas chromatograph equipped with a Disc integrator.

To determine temperature accurately, a thermocouple used in conjunction with a temperature potentiometer was inserted into a thermocouple well which extended directly into the heated portion of the pyrolysis tube.[5] Samples were contained in quartz

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(5) These refinements were made to conduct quantitative experiments for a related project.

microtubes rather than combustion boats to avoid the temperature drop encountered when the half-gram boats were introduced into the small furnace. Sample tubes were introduced into the furnace with a hand-operated "pusher" which afforded more positive control than the magnet controlled pusher provided with the equipment. A constant-voltage transformer was employed to provide maximum furnace temperature stability.

Pyrolysis of samples was accomplished as follows. The entire apparatus was flushed with helium. After the furnace was heated to temperature and allowed to equilibrate, the sample was thrust into the heated zone with the pusher. Pyrolysis was almost instantaneous and the pyrolysate was swept by helium flow (2 ml/sec) through the heated (400°)[6] glass connecting tube into the temperature-programmed (11° or 21°/min.) chromatograph. The chromatograph port was maintained at 400°[6] to prevent condensation. The most suitable packing found for the chromatograph column was 3% SF- (silicone fluid) 1093 (a General Electric product) on 70/80 mesh, acid-washed, DMCS-treated Chromosorb G. A 7-ft column with this packing is suitable for programming to at least 400° (dual column use) and affords good separation with elution at comparatively low temperatures. Samples for infrared spectra were obtained by condensing pure components as they were eluted from the column.

Benzophenone Azine.—Forty grams of calcium oxide were added to a solution of 36.4 g of benzophenone and 35.4 g of hydrazine hydrate (99–100%) in 300 ml of ethanol. After the mixture was heated under reflux for 18.5 hr, the mixture was filtered hot and the filtrate was concentrated by evaporation to a volume of 75 ml. Cooling and agitation afforded crystals of benzophenone hydrazone which, after washing with 50 ml of cold ethanol and drying, weighed 29.2 g and melted at 96–98.5° (lit.[7] mp 97–98°).

Thirty-eight grams (0.096 mole) of benzophenone hydrazone was dissolved in 1 l. of ethanol and to this was added 10.6 g of sulfuric acid which had been diluted with an equal volume of water. The mixture was allowed to stand overnight and then filtered to obtain a mixed precipitate of benzophenone azine and hydrazine sulfate. After the latter compound was removed by a thorough washing with water, 31.5 g (91% yield) of benzophenone azine, mp 161.7–163.7°, remained. One recrystallization from the minimum quantity of *n*-propyl alcohol afforded 27.5 g (87% recovery) of needles, mp 162.8–163.8° (lit.[7] mp 164°).

6-Phenylphenanthridine.[8]—A solution of 0.6 ml of anhydrous stannic chloride in 5 ml of nitrobenzene was added to a rapidly boiling solution of 8.45 g (0.05 mole) of 2-aminobiphenyl in 45 ml of nitrobenzene. Benzotrichloride (8 ml, 0.0575 mole) was then immediately added and the reaction mixture was heated under reflux for 90 min, after which period most of the solvent was removed by vacuum distillation. Rather than to attempt to induce crystallization in the black tar which resulted, a portion of it was dissolved in methylene chloride and several milligrams of 6-phenylphenanthridine were collected by gas chromatography of the solution. The infrared spectrum of this material was identical with that resulting from benzophenone azine pyrolysis.

Benzhydrylidene–Benzylidene Azine.—A mixture of 13.2 g of benzaldehyde, 24.0 g of benzophenone hydrazone, 60.0 g of freshly calcined calcium oxide, and 300 ml of ethanol was heated under reflux for 24 hr. The hot suspension was filtered and the filtrate was concentrated to 90-ml volume by evaporation. The solution was set aside to crystallize. Seventeen grams (48% yield) of benzhydrylidene–benzylidene azine, mp 73.5–75.0°, was recovered. The sample was recrystallized once from hexane, then twice from ethanol to afford 8 g (47% recovery) of pure material, mp 75.6–76.1° (lit.[9] mp 75°).

Identification of Triphenylethylene in the Pyrolysate from Benzhydrylidene–Benzylidene Azine.—Careful comparison of the gas chromatograms from the benzophenone azine pyrolysis (Figure 1) and the mixed azine pyrolysis (Figure 2) reveals that the peak attributed to triphenylethylene $[(C_6H_5)_2C{=}CHC_6H_5]$ in the latter (Figure 2) could be due to benzhydrylideneaniline $[(C_6H_5)_2C{=}NC_6H_5]$.

These two molecules are extremely similarly constituted, are not resolved by the gas chromatograph, and were both expected to be formed from the pyrolysis of the mixed azine. Even the infrared spectra are so alike that samples of a mixture of the two cannot be identified easily by this means. Since the presence or absence of triphenylethylene in the pyrolysate was the key point in interpretation of the mechanism, it was necessary to be certain of its identity.

Known samples (5 mg) of triphenylethylene and benzhydrylideneaniline in 1-ml portions of carbon tetrachloride were treated with chlorine gas for 2.0 min and then allowed to stand at room temperature for 5.0 min. After solvent was removed in a stream of nitrogen until 40–50 μl remained, the samples were injected into the temperature-programmed gas chromatograph (silicone oil column). The identical experiment was performed with that portion of the collected eluate from gas chromatography of the benzhydrylidene–benzylidene azine pyrolysate corresponding to the combined peak triphenylethylene–benzhydrylideneaniline. Comparison of the chromatogram with those from the known samples revealed that the principal component was triphenylethylene. This is consistent with the relatively large peak due to its presence (Figure 2) since only half the quantity of benzhydrylideneaniline would be expected in the pyrolysate from the mixed azine as in that from benzophenone azine.

Registry No.—II, 983-79-9; V, 2720-93-6; VI, 13118-38-2.

Acknowledgments.—Support by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio (Contract Number AF 33(657)11163), is acknowledged. The technical assistance of Mr. G. K. Ragep is appreciated.

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(6) A temperature of 375° was used in the lowest temperature experiment.

(7) H. H. Szmant and C. McGinnis, *J. Am. Chem. Soc.*, **72**, 2890 (1950).

(8) H. J. Barber, L. Bretherich, T. M. Eldridge, S. J. Holt, and W. R. Wragg, *J. Soc. Chem. Ind.*, **69**, 82 (1950).

(9) T. Curtins and F. Routerberg, *J. Prakt. Chem.*, [2] **44**, 192 (1891).