material and the solvent, the product formed in each case was recrystallized from suitable solvents.

Oxidation of phenylhydrazine (2 g, 0.019 mol) gave a mixture of biphenyl (0.75 g, 26%), mp 70°, and azobenzene (40 mg, 3%), mp 65°.

p-Nitrophenylhydrazine (2 g, 0.013 mol) gave *p*-nitrobiphenyl (1.3 g, 50%), mp 113°, after recrystallization from ethanol.

2,4,6-Trichlorophenylhydrazine (2 g, 0.009 mol) on oxidation gave 2,4,6-trichlorobiphenyl (0.9 g, 39%), mmp 62°[31] after recrystallization from dilute acetic acid.

Oxidation of Hydrazines.—In a typical experiment a mixture of the hydrazine and manganese dioxide (1:2.5) in 75 ml of dry benzene was stirred at room temperature for 1 hr. The products were purified by chromatography over alumina using benzene and by recrystallization from suitable solvents.

N-Aminopiperidine (2.5 g, 0.025 mol) gave 1.9 g (76%) of 1,4-bispentamethylenetetrazene (XVI): mp 44° after recrystallization from dilute ethanol; uv spectrum of XVI (cyclohexane), λ_{max} 288 mμ (ϵ, 11,630); ir spectrum (KBr), ν_{max} 2930, 2800, 1460, 1442, 1365, 1320, 1290, 1265, 1160, 1125, 1082, 1066, 1030, 1025, 986, 970, 925, 868, 770, and 695 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}N_4$: C, 61.2; H, 10.2; N, 28.5. Found: C, 60.8; H, 10.6; N, 28.4.

Oxidation of N-aminohomopiperidine (3 g, 0.026 mol) gave 2.5 g (86%) of 1,4-bishexamethylenetetrazene (XVII), which melted at 62–63° after recrystallization from ethanol: uv spectrum of XVII (cyclohexane), λ_{max} 290 mμ (ϵ 12,610); ir spectrum (KBr), ν_{max} 2930, 2850, 1460, 1442, 1365, 1280, 1240, 1200, 1120, 1110, 1070, 1060, 1005, 986, 965, 912, 885, 865, 820, and 715 cm^{-1}.

Anal. Calcd for $C_{12}H_{24}N_4$: C, 64.28; H, 10.7; N, 25.0. Found: C, 64.06; H, 10.30; N, 25.14.

N-Aminomorpholine (2 g, 0.019 mol) of oxidation gave 1.6 g (80%) of 1,4-bis(3-oxapentamethylenetetrazene (XVIII): mp 157° after recrystallization from ethanol: uv spectrum of XVIII (cyclohexane), λ_{max} 284 mμ (ϵ 10,150); ir spectrum (KBr), ν_{max} 3000, 2910, 1460, 1400, 1380, 1275, 1220, 1190, 1140, 1120, 1100, 1080, 1020, 990, 935, 870, and 779 cm^{-1}.

Anal. Calcd for $C_8H_{16}O_2N_4$: C, 48.0; H, 8.0; N, 28.0. Found: C, 48.04; H, 8.2; N, 28.09.

N,N-Diphenylhydrazine (0.6 g, 0.003 mol) gave 0.45 g (76%) of 1,1,4,4-tetraphenyltetrazene: mp 123° dec (lit.[32] mp 123°); uv spectrum (cyclohexane), λ_{max} 285 mμ (ϵ 13,900), 304 (15,140) and 360 (14,860); ir spectrum (KBr), ν_{max} 3010, 1590, 1490, 1450, 1345, 1325, 1295, 1090, 1280, 1010, 1100, 1065, 1020, 995, 938, and 890 cm^{-1}.

Anal. Calcd for $C_{24}H_{20}N_4$: C, 79.1; H, 5.9; N, 15.3. Found: C, 79.29; H, 5.6; N, 15.0.

Oxidation of N,N-Dibenzylhydrazine.—N,N-Dibenzylhydrazine (0.5 g, 0.0024 mol) was treated with manganese dioxide (2.2 g) in chloroform (50 ml) at room temperature for 1 hr. Removal of the unchanged manganese dioxide gave a product which was chromatographed over alumina. Elution with petroleum ether (bp 60–80°) and recrystallization from ether gave 15 mg (10%) of 1,1,4,4-tetrabenzyltetrazene, mmp 99°. Further elution of the alumina column with a mixture of benzene and petroleum ether gave 85 mg (20%) of bibenzyl, mmp 52°.

In a second experiment, a mixture (0.5 g, 0.0024 mol) of N,N-dibenzylhydrazine and 1.8 g of manganese dioxide was refluxed in absolute ethanol (70 ml) for 1 hr. Work-up of the mixture in the usual manner gave 0.21 g (49%) of bibenzyl, mmp 52°. None of the tetrazene could be isolated from this run.

Registry No.—Manganese dioxide, 1313-13-9; *o*-phenylenediamine, 95-54-5; *p*-phenylenediamine, 106-50-3; N-phenyl-*p*-phenylenediamine, 101-54-2; N,N′-diphenyl-*p*-phenylenediamine, 74-31-7; 2,2′-diaminobiphenyl, 1454-80-4; 2,2′-diaminobiphenyl sulfide, 5873-51-8; XI, 16504-18-0; XII, 16504-19-1; XIII, 1050-82-4; benzophenone anil, 574-45-8; phenylhydrazine, 100-63-0; *p*-nitrophenylhydrazine, 100-16-3; 2,4,6-trichlorophenylhydrazine, 5329-12-4; N-aminopiperidine, 2213-43-6; XVI, 2081-14-3; N-aminohomopiperidine, 5906-35-4; XVII, 16504-24-8; N-aminomorpholine, 4319-49-7; XVIII, 16504-26-0; N,N-diphenylhydrazine, 530-50-7; 1,1,4,4-tetraphenyltetrazene, 16504-27-1; N,N-dibenzylamine, 5802-60-8.

Acknowledgment.—The authors thank Mr. A. H. Siddiqui for his help in microanalysis.

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[31] P. J. Bain, E. J. Blackman, and W. Cummings, *Proc. Chem. Soc.*, 186 (1962).

[32] H. Wieland and E. Wecker, *Ber.*, **43**, 3265 (1910).

Some Aspects of Vinyl Azide Chemistry. Thermally Induced Reactions

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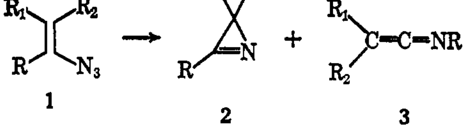
A comparison of the chemistry of terminal and internal vinyl azides is presented. On decomposition, internal vinyl azides formed azirines while terminal vinyl azides did not. The nature of the products from the latter azides depended upon the substituents on the carbon β to the azido group. In solvents other than ethanol, 9-(azidomethylene)fluorene gave 9-(N,N-fluorenylideneaminomethylene)fluorene, while 2-azido-1,1-diphenylethylene and 1-azido-2-phenylpropene formed indole derivatives. The latter two compounds when decomposed in ethanol produced dihydropyrazines at the expense of indole formation. Possible mechanisms for these reactions are considered. In addition, the geminal vinyl diazide, 9-diazidomethylenefluorene, was found to form 9-azido-9-fluorenecarbonitrile while the vicinal diazide, 2,3-diazido(N-phenyl)maleimide, gave N,N-bis(cyanocarbonyl)aniline.

The decomposition of vinyl azides has been the subject of several recent investigations.[1] The majority of these studies has dealt exclusively with internal[2] vinyl azides 1. It was found that on photolysis or thermolysis this type of azide consistently lost nitrogen and rearranged to azirines 2 in good yield usually accompanied by small amounts of iminoketenes 3.[1a–c]



1 2 3

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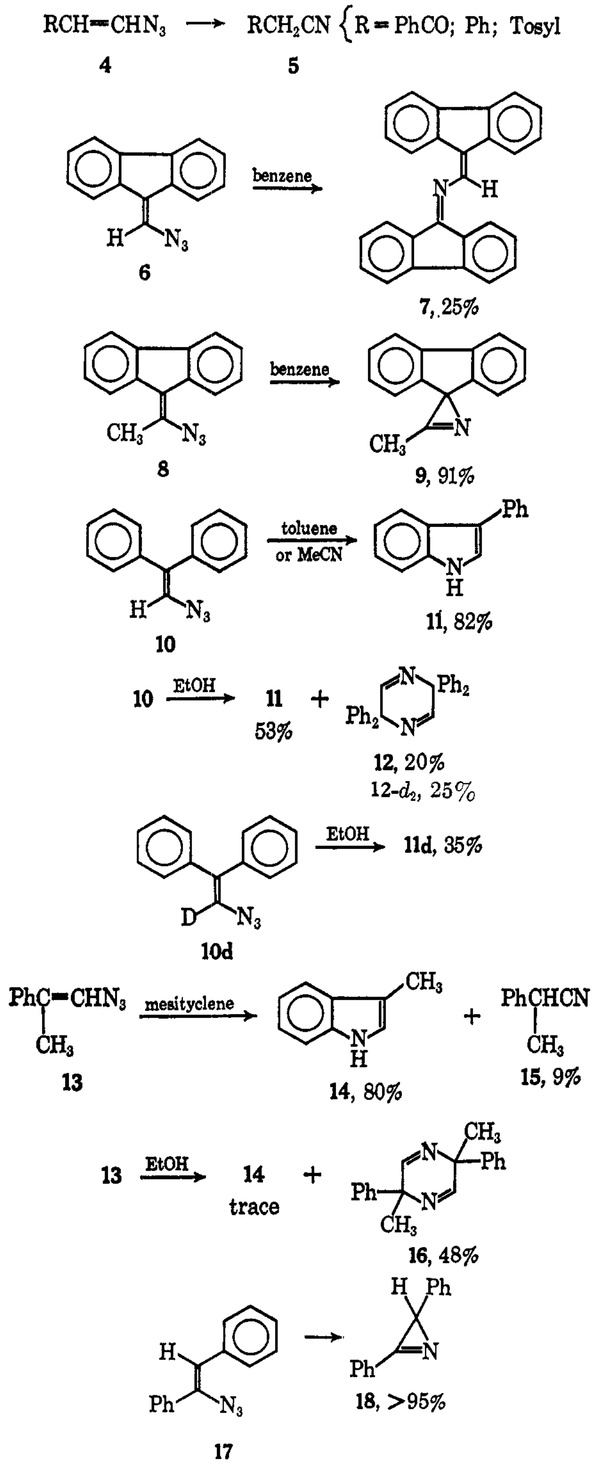
[1] G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962); (b) A. Hassner and F. W. Fowler, *Tetrahedron Lett.*, in press; (c) G. R. Harvey and K. W. Ratts, *J. Org. Chem.*, **31**, 3907 (1966); (d) S. Maiorana, *Ann. Chim.* (Rome), **56**, 1531 (1966); (e) J. H. Boyer, W. E. Krueger, G. J. Mikol, *J. Amer. Chem. Soc.*, **89**, 5504 (1967); (f) J. S. Meek and J. S. Fowler, *J. Org. Chem.*, **32**, 985 (1968).

[2] By internal, we mean vinyl azides in which a substituent other than hydrogen is bonded to the carbon bearing the azide group. When a hydrogen atom is bonded to the azide bearing carbon, we will refer to the compound as a terminal vinyl azide.

The few previous studies on the decomposition of terminal vinyl azides indicated that the products of these reactions were not so easily predicted. Some evidence was obtained for the intermediacy of an azirine (2, R = R_1 = H; R_2 = tosyl) in the photodecomposition of β-azidovinyl *p*-tosyl sulfone (**4**, R = tosyl).[1f] However, thermal decomposition of the three terminal vinyl azides **4** was reported to yield nitriles **5** with no accompanying azirine formation.[1d-f]

In the present study we have prepared and thermally decomposed a number of terminal vinyl azides (see Chart I). Whenever possible we have also prepared a corresponding internal vinyl azide derivative for comparison. We found, as did the other workers,[1] that internal vinyl azides always produced azirines. On the other hand, the terminal compounds did not, but instead a variety of products resulted depending on the constitution of the molecule. For example, heating 9-(azidomethylene)fluorene (**6**) in benzene for several hours produced about 25% of a high melting, red crystalline material having the formula $C_{27}H_{17}N$ along with a considerable amount of tar. A high resolution mass spectrometric analysis of this red material suggested to us that it was 9-(N,N-fluorenylidenaminomethylene)fluorene (**7**). This compound was synthesized by bromine oxidation of the condensation product of 9-aminofluorene and 9-fluorenecarboxaldehyde and found to be identical with the red reaction product. In contrast with the results for decomposition of the terminal azide **6**, the corresponding internal azide, 9-(1-azidoethylidene)fluorene (**8**), produced the expected azirine, 2-2-(2,2′-biphenylene)-3-methyl-2H-azirine (**9**).

CHART I
A SUMMARY OF PRODUCTS
OBTAINED FROM THERMOLYSIS OF VINYL AZIDES

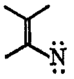


When the terminal azide, 2-azido-1,1-diphenylethylene (**10**), the diphenylmethane analog of fluorene derivative **6**, was decomposed in xylene or acetonitrile, approximately 80% of 3-phenylindole (**11**) was isolated from the reaction. However, when the decomposition was carried out in ethanol, only 53% of indole **11** was obtained, but now 20% of 2,2,5,5-tetraphenyldihydropyrazine (**12**) was also isolated. The structure of the latter material was established by a synthesis in which 2-chloro-2,2-diphenylacetaldehyde was heated in an ammoniacal ethanol solution. Our attempts to synthesize the corresponding methyl-substituted internal vinyl azide by methods analogous to those used in the preparation **10** and **13** failed.

On thermolysis, the behavior of 1-azido-2-phenylpropene (**13**) was found to be quite similar to that found for **10**. Decomposition of **13** in boiling mesitylene produced an 80% yield of 3-methylindole (**14**) accompanied by a small quantity of α-phenylpropionitrile (**15**). Changing the solvent from mesitylene to ethanol caused a pronounced effect: 48% 2,5-dimethyl-2,5-diphenyldihydropyrazine (**16**) was formed along with a trace of indole **14**; no nitrile **15** was formed.

The results reported in this paper demonstrate that the substituent on the carbon atom bearing the azido group determines whether or not azirine is formed in the thermally induced reactions. However, the nature of nonazirine-forming reactions is very much influenced also by the substituents on the β carbon of the terminal vinyl azide. For example, in the series 2-azido-1,1-diphenylethylene (**10**), 1-azido-2-phenylpropene (**13**), and β-styryl azide (**4**, R = Ph) thermolysis leads to 0, 9, and 74% H-migration product accompanied by 82, 80, and 0% insertion into an aromatic C–H bond, respectively. Moreover, the fact that α-azido-*trans*-stilbene (**17**) decomposed to 2,3-diphenyl-2H-azirine (**18**) in high yield[1b] with little if any accompanying indole formation shows clearly that indole does not result merely as a consequence of a *cis* relationship between the phenyl and azido groups. In addition, reactions in ethanol favored dimerization to dihydropyrazines at the expense of indole formation.

In considering a mechanistic rationale for vinyl azide chemistry one is strongly tempted to invoke a vinyl nitrene intermediate. Such a species in either its singlet **19** or triplet state **20** could lead to all the prod-



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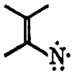

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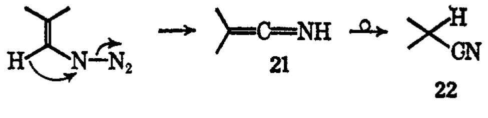
ucts found from photolytically or thermally induced fragmentation reactions of vinyl azides. Starting from a vinyl nitrene one can write reasonable mechanisms leading to azirine, iminoketene, indole, or dihydropyrazine. Unfortunately equivalent mechanistic pathways can be envisioned assuming that a thermally excited vinyl azide undergoes rearrangement and loss of molecular nitrogen concertedly. However, neither the vinyl nitrene nor azide mechanism implicates the substituent on the azide-bearing carbon atom and at least to this extent they are both unsatisfactory. Neither is any mechanism satisfactory which involves cleavage or the α-carbon–hydrogen bond in terminal vinyl azides. This was established by decomposing deuterated terminal vinyl azide **10d** in ethanol, and showing that all the deuterium remained bonded to the original nitrogen-bearing carbon atom. The observed increase in dihydropyrazine over indole when **10** and **13** were decomposed in ethanol rather than in a hydrocarbon solvent seems to imply the intermediacy of a highly polar species in dihydropyrazine formation. However, this explanation appeared less likely when it was found that decomposition of **10** in acetonitrile gave results identical with those found for decomposition in xylene. It may be that dihydropyrazines result from extremely mild proton-catalyzed decomposition of **10** and **13**. Unfortunately addition of even trace amounts of acetic or toluenesulfonic acid to the solutions of **10** in either benzene or acetonitrile gave intractable product mixtures. Similarly, decomposition of **10** in 2-propanol or *t*-butyl alcohol gave a tarry product from which it proved possible to isolate only 30–50% indole **11**.

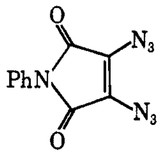
An explanation for the production of nitriles from terminal vinyl azides **4** is found in a mechanism analogous to that for the Curtius rearrangement of acid azides to isocyanates (Scheme I) and is consistent with the production of N-substituted iminoketenes from the decomposition of internal vinyl azides. The iminoketene **21** first obtained is certainly more stable in its tautomeric nitrile form **22**. Unfortunately we are unable to explain why this Curtius-like rearrangement should range all the way from a principal to an insignificant reaction pathway in the thermolysis of terminal vinyl azides.

SCHEME I



In the course of this study we prepared a vicinal and a geminal vinyl diazide. The thermally induced decomposition of these compounds shed no light on the mechanism of vinyl azide decompositions but did give interesting results. Vicinal vinyl diazide 2,3-diazido-(N-phenyl)maleimide (**23**), when heated in benzene, formed N,N-bis(cyanocarbonyl)aniline (**24**) in 83% yield. This result is in keeping with the findings of Hall and Paterson[3] on the thermolysis of 1,2-diazidobenzene and naphthalene derivatives, in which loss of the two molecules of nitrogen is accompanied by ring opening of the aromatic nucleus with production of dinitriles.

The labile[4] geminal diazide, 9-diazidomethylenefluorene (**25b**), is presumed to be an intermediate in the reaction of 9-dichloromethylenefluorene (**25a**) with azide ion. However, even at room temperature the only product isolated from this reaction was 9-azido-9-fluorenecarbonitrile (**26**). This compound exhibited strong infrared absorption characteristic of an azide group but no absorption for a nitrile group. Since the intensity of the band for various types of nitriles ranges from strong to undetectable,[5] additional proof of the structure of **26** was obtained by its thermolysis in chlorobenzene to 10-cyanophenanthridine (**27**) in 83% yield. This result is analogous to the conversion of 9-aryl-9-azidofluorenes into 10-arylphenanthridines.[6]



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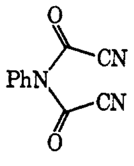

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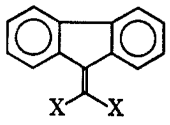
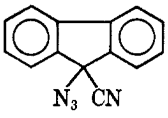


25a, X = Cl
b, X = N₃



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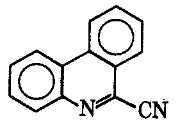

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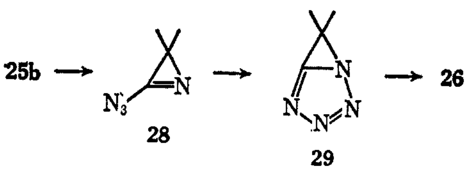
A reasonable mechanistic explanation for the formation of cyanoazide **26** from diazide **25b** is given in Scheme II. The proposed isomerization of **28** to **29** is a well-known type of rearrangement reaction. The resulting tetrazole **29** is certainly a highly strained molecule which finds relief in opening to **26**.

SCHEME II



Experimental Section[7]

9-(Azidomethylene)fluorene (6).—Sodium azide (5.2 g, 0.08 mol) was added to an ice-cold solution of 10 g (0.04 mol) of 9-bromomethylenefluorene[8] in 200 ml of dimethylformamide. The resulting mixture was stirred under a nitrogen atmosphere and cooled in an ice bath for 3 hr, after which it was placed in a refrigerator for 70 hr and swirled occasionally. The mixture was poured onto ice, diluted with ice–water and extracted with methylene chloride. The methylene chloride phase was washed six times with ice–water, dried (K_2CO_3), and evaporated at reduced pressure without external heating. The orange crystal-

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[3] J. H. Hall and E. Patterson, *J. Amer. Chem. Soc.*, **89**, 5856 (1967).

[4] By working at less than 5° it was possible to isolate a substance believed to be **25b**, but this material decomposed to a tarry mass at room temperature.

[5] R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

[6] L. A. Pinck and H. E. Hilbert, *J. Amer. Chem. Soc.*, **59**, 8 (1937).

[7] All melting points are correct. Boiling points are uncorrected.

[8] D. F. DeTar, E. Broderick, G. Foster, and B. D. Hilton, *J. Amer. Chem. Soc.*, **72**, 2183 (1950).

line residue weighed 8.9 g and showed strong absorption in the infrared spectrum ($CHCl_3$) at 4.70 (azide) and 6.1 μ (C═C).[1b]

Conversion of 9-Azidomethylenefluorene (6) into 9-(N,N-Fluorenylidenaminomethylene)fluorene (7).—A deaerated solution of 2 g (9.1 mmol) of vinyl azide **6** in 50 ml of benzene was maintained at reflux in a nitrogen atmosphere for 3 hr. The gummy red solid obtained on evaporation of the benzene was recrystallized from a small quantity of benzene to give 0.4 g (25%) of **7**. Several additional recrystallizations from benzene gave shiny red needles of mp 324–326°. High resolution mass spectrometry confirmed the molecular formula of $C_{27}H_{17}N$, while the assigned structure was established definitively by comparison of melting point and infrared spectrum with that of independently synthesized material (see below).

9-(N,N-Fluorenylidenaminomethyl)fluorene (7).—To a deaerated solution of 193 mg (1 mmol) of 9-fluorenecarboxaldehyde[9] in 30 ml of pyridine was added 217 mg (1 mmol) of 9-aminofluorene hydrochloride. The resulting mixture was boiled for 3 hr in a nitrogen atmosphere after which the solution was cooled, swirled over anhydrous K_2CO_3, filtered, and evaporated to dryness. The semicrystalline orange residue was warmed with a small volume of benzene and cooled, and the insoluble portion was collected. This material weighed 200 mg (55%) and decomposed to a red oil at 225–230°.

To a solution of 178 mg (0.5 mmol) of the above condensation product in 15 ml of pyridine was added dropwise 0.5 mmol of bromine dissolved in pyridine (0.117 g/ml). The reaction turned bright red and a precipitate formed after a few minutes. After a half hour, the orange precipitate was collected, washed with benzene, and dried (Na_2SO_4) to give 90 mg (50%) of **7**, mp 322–325°. Several additional recrystallizations from benzene gave shiny red needles, mp 324–326°.

Anal. Calcd for $C_{27}H_{17}N$: C, 91.24; H, 4.82; N, 3.94. Found: C, 91.0; H, 4.8; N, 4.4.

9-(1-Bromoethylidene)fluorene.—Ethyl α-fluorenylidenepropionate [bp 188 (1.4 torr), mp 65–69°] was prepared in 70% yield by a Reformatsky condensation of fluorenone and ethyl α-bromopropionate in benzene solution following the procedure of Sieglitz and Jassoy[10] for the preparation of ethyl fluorenylideneacetate. In the present case it was found necessary to initiate the reaction by the addition of a small amount of magnesium and iodine.

The fluorenylidenepropionate was saponified by heating an aqueous ethanolic potassium hydroxide solution for 20 min in a nitrogen atmosphere. The acid was precipitated by the addition of hydrochloric acid, collected, and dried overnight in a vacuum oven at 60°. The crude acid was pulverized, suspended in carbon tetrachloride, and stirred 48 hr under nitrogen in the dark with 1 equiv of bromine. The residue remaining after evaporation of the solvent at reduced pressure, was boiled for 2 hr with a slight excess of 0.5 *N* sodium hydroxide. The bromide was extracted from the aqueous alkaline mixture with benzene. The crude bromoethylidenefluorene was sublimed (yield based on ester was 50%) and recrystallized from cyclohexane to give pale yellow crystals, mp 90–91°.

Anal. Calcd for $C_{15}H_{11}Br$: C, 66.42; H, 4.09; Br, 29.49. Found: C, 66.3; H, 4.0; Br, 29.8.

9-(1-Azidoethylidene)fluorene (8).—9-(1-Bromoethylidene)fluorene was converted into the corresponding azide **8** with sodium azide in cold dimethylformamide as described above for the preparation of 9-(azidomethylene)fluorene (**6**). Crude **8** (pale yellow crystals) exhibited a strong split azide band in the infrared spectrum ($CHCl_3$) at 4.67 and 4.82 and C═C absorption at 6.15 μ.[1b]

Conversion of 9-(1-Azidoethylidene)fluorene (8) into 2,2-(2,2′-Biphenylene)-3-methyl-2H-azirine (9).—A benzene (20 ml) solution of 650 mg (2.8 mmol) of **8** was maintained at reflux in a nitrogen atmosphere for 2 hr after which the solvent was removed at reduced pressure and the residue transferred to a sublimer and heated at 100° (0.05 torr). The sublimate (590 mg 91%) had mp 86–88°. Recrystallization from methanol gave material of mp 97–99°. The infrared spectrum (CCl_4) exhibited the azirine, C═N, absorption at 5.6 μ. The nmr spectrum (CCl_4) showed a singlet at δ 2.51 and a multiplet centered at 7.1 in the ratio of 3:8.

Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.6; H, 5.2; N, 7.1.

2-Azido-1,1-diphenylethylene (10).—A mixture of 1.3 g (20 mmol) of sodium azide in 75 ml of methanol containing 2 g (10 mmol) of dissolved 1,1-diphenylethylene oxide[11] was stirred at reflux in a nitrogen atmosphere for 24 hr, after which the reaction was cooled and the solvent removed at reduced pressure. The residue was distributed between water and ether. The ether layer was dried (K_2CO_3) and evaporated at reduced pressure. The colorless, oily residue weighed 1.75 g and exhibited strong infrared absorption at 4.75 (azide) and 3.25 μ (hydroxyl).

Using the method of Hazen and Rosenburg[12] 2.0 g (8.4 mmol) of crude 1,1-diphenyl-2-azidoethanol was dehydrated in dimethylformamide-pyridine solution with methanesulfonyl chloride containing dissolved sulfur dioxide. The work-up consisted of dropwise addition of 25 ml of water to the ice bath cooled reaction mixture (temperature maintained below 30°) followed by addition of a large excess of water. The resulting aqueous mixture was twice extracted with methylene chloride. The methylene chloride solution was washed successively with cold dilute sulfuric acid, cold dilute carbonate solution, and water and then dried (Na_2SO_4) and evaporated to dryness at reduced pressure. The yellow, oily residue was taken up in petroleum ether (30–60°) and chromatographed on a 20-g silica gel column. The 1,1-diphenyl-2-azidoethylene (**10**) (950 mg 50%) was eluted with 1:1 petroleum ether–benzene and exhibited strong absorption in the infrared spectrum (neat) at 4.72 (azide) and 6.2 μ (C═C).[1b] Nmr (CCl_4) absorption was as follows: multiplets at δ 7.26 and 7.16 totaling ten protons and a singlet of one proton at 6.48.

Thermolysis of 2-Azido-1,1-diphenylethylene (10). A. In Xylene.—A solution of 1.2 g (4.5 mmol) of azide **10** in 25 ml of xylene was maintained at reflux in a nitrogen atmosphere for 22 hr. The residue obtained on evaporation of the xylene at reduced pressure was transferred to a sublimer and heated to 95° (0.001 torr) for several hours. The sublimate weighed 970 mg (82%) and had mp 76–79°. One recrystallization from benzene gave material of mp 88–89°. The picrate melted at 106–107°. Bettembourg and David[13] reported mp 86–88° for 3-phenylindole (**11**) and 107–109° for the picrate.

B. In Acetonitrile.—The only identifiable product was 3-phenylindole (**11**, 75%).

C. In Ethanol.—A solution of 260 mg (1.2 mmol) of azide **10** in 25 ml of ethanol was boiled in a nitrogen atmosphere for 16 hr during which time a slight precipitate formed. The solvent was removed at reduced pressure and the residue transferred to a sublimer and heated at 95° (0.001 torr) for several hours. The sublimate (53%) was identified as 3-phenylindole (**10**) by comparison of its infrared spectrum with that of authentic material. The residue (20%) was recrystallized several times from benzene–hexane to give material of mp 277–278° which was not depressed when admixed with authentic 2,2,5,5-tetraphenyldihydropyrazine (**12**).

2,2,5,5-Tetraphenyldihydropyrazine (12).—2-Chloro-2,2-diphenylacetaldehyde[14] (1 g, 5.3 mmol) in 4 ml of ether was added dropwise to a stirred, ice bath cooled solution of 1 g of ammonia in 15 ml of ethanol. After addition was complete, the reaction solution was stirred at room temperature for 2 hr and then boiled under nitrogen overnight. Crystals began to separate after several hours. The cooled reaction mixture was filtered and the crystals were collected (0.28 g, 33%). Recrystallization from benzene–hexane gave **12**, mp 277–278°.

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.1; H, 5.9; N, 7.2.

A high resolution mass spectrometric analysis was in agreement with the above assigned structure in that the parent peak had a mass in agreement with the formula $C_{28}H_{22}N_2$ and the major fragments had masses corresponding to the following formula: $C_{27}H_{21}N$, $C_{21}H_{16}N$, $C_{15}H_{11}N$, $C_{14}H_{11}N$, $C_{14}H_{10}N$.

2-Azido-1,1-diphenylethylene-2-d_1 (10-*d*).—A solution of 50 g (0.78 mol) of commercially available acetic acid-d_4 in 40 ml of methanol containing 1 ml of sulfuric acid was allowed to stand at room temperature overnight. A fractionation of this solution

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[9] Prepared by the method of W. Wislicenus and M. Waldmuller [*Ber.*, **42**, 785 (1909)], except that sodium hydride in tetrahydrofuran was substituted for potassium dissolved in ethanol.

[10] A. Sieglitz and H. Jassoy, *Ber.*, **54**, 2133 (1921).

[11] S. J. Cristol, J. R. Douglass, and J. S. Meek, *J. Amer. Chem. Soc.*, **73**, 816 (1951). It was found that a temperature of 5–10° gave better results than 0° during bromohydrin formation.

[12] G. G. Hazen and D. W. Rosenburg, *J. Org. Chem.*, **29**, 1931 (1964).

[13] M. C. Bettembourg and S. David, *Bull. Soc. Chim. Fr.*, 772 (1962).

[14] D. Y. Curtain, J. A. Kompmeier, and B. R. O'Connor, *J. Amer. Chem. Soc.*, **87**, 875 (1965).

through a 2-ft spinning-band column gave 61 g of material boiling at 53.5° which was shown by an nmr analysis to consist of a mixture of 64 mol % methyl acetate-d_3 and methanol.

The total methyl acetate-d_3–methanol mixture was added to 2 mol of phenyl magnesium bromide in ether and the resulting methyl-d_3-benzhydrol was isolated in the usual way. Recrystallization from 95% ethanol gave 85 g of the benzhydrol, mp 80–81° (lit.[15] mp 81°).

To a solution of 20 g (0.1 mol) of the benzhydrol-d_3 in 100 ml of warm (50–60°) 80% aqueous acetic acid was added dropwise 16 g (0.1 mol) of bromine in 10 ml of acetic acid. After an initial induction period warming was discontinued and bromine was rapidly consumed. When addition was complete, the reaction was diluted with benzene, washed well with water, dried (Na_2SO_4), and evaporated to dryness. The crystalline bromohydrin-d_2 was recrystallized from hexane (mp 73–75°) and converted into 1,1-diphenylene oxide-d_2 by the method of Cristol, Douglass, and Meek.[11] The 2-azido-1,1-diphenylethylene-2-d_1 (**10**-*d*) was prepared as described above for 2-azido-1,1-diphenylethene (**10**). The nmr spectrum of the deuterium compound exhibited phenyl proton absorption at δ 7.18 and 7.26 and at most 1% vinyl proton absorption. The infrared spectrum (neat) showed N_3 absorption at 4.7 μ.

Thermolysis of 2-Azido-1,1-diphenylethylene-2-*d*₁ (10-*d*) in Ethanol.—A solution of 1.8 g (0.008 mol) of the deuterated vinyl azide **10**-*d* in 50 ml of ethanol was maintained at reflux in a nitrogen atmosphere for 16 hr. 2,2,5,5-Tetraphenyldihydropyrazine-3,6-d_2 (**12**-*d*, 400 mg, 25%; mp 275–276°) was collected by filtration and its deuterium content was established by mass spectrometry (*m/e* 388).

The oily residue obtained on evaporation of the filtrate was transferred to a sublimer and heated at 90–100° (0.001 torr). The crystals collected on the cold finger weighed 610 mg (38%). Recrystallization from hexane gave 3-phenylindole-2-d_1 (**11**-*d*), mp 87.5–88° which was not depressed on admixture with authentic 3-phenylindole. The deuterated compound had an identical ultraviolet spectrum but different nmr and infrared spectra from that of fully protonated 3-phenylindole.

1-Azido-2-phenylpropene (13).—1-Methyl-1-phenylethylene oxide[11] was allowed to react with sodium azide as described above for the preparation of 2-azido-1,1-diphenylethylene (**10**). The almost colorless, oily, crude 2-azido-1-methyl-1-phenylethanol showed absorption in the infrared spectrum (neat) at 4.7 (azide) and 2.8 μ (hydroxyl).

The crude azidomethylphenylethanol (11 g, 0.062 mol) was dehydrated by the method of Hazen and Rosenburg[12] as described above for the preparation of the azidodiphenylethylene **10**. In this way 2.5 g (25%) of **13** was obtained having the following properties: infrared spectrum (neat) showed absorption at 4.72 (azide) and 6.12 μ (C=C);[1b] the nmr spectrum (CCl_4) showed phenyl absorption at δ 7.20 with a multiplet at 6.25 (vinyl hydrogen) and a slightly split methyl absorption at 1.95. On decoupling, the methyl doublet collapsed to a singlet while the multiplet at δ 6.25 became two singlets at 6.18 and 6.27 with a ratio of 1:7.

Thermolysis of 1-Azido-2-phenylpropene (13). A. In Mesitylene.—To 20 ml of boiling mesitylene, under nitrogen, was added 1.2 g (76 mmol) of **13**. After 14 hr, the solvent was evaporated at reduced pressure and the residue was transferred to a sublimer and heated for several hours at 80–100° (0.2 torr). The white, crystalline sublimate weighed 870 mg (89%) and was shown by glpc analysis (6 ft × 0.125 in. UCON POLAR 2000 on 80/100 acid-washed Chromosorb W), using authentic compounds as standards, to consist of a 1:9 mixture of 2-phenylproprionitrile (**15**) and 3-methylindole (**14**). Pure **14** was obtained by recrystallization of the sublimate from benzene–hexane.

B. In Ethanol.—A solution of 1.4 g (0.0088 mol) of azide **13** in 50 ml of deaerated ethanol was boiled in a nitrogen atmosphere for 20 hr. The solvent was removed at reduced pressure and the residue was heated at 50–60° (0.001 torr) in a sublimer. A small quantity of liquid collected on the cold finger; this contained some 3-methylindole (**14**) as shown by glpc analysis. Raising the bath temperature to 100–110° caused a solid to collect (550 mg, 48%). This was recrystallized from benzene–hexane and resublimed to give pure 2,5-dimethyl-2,5-diphenyldihydropyrazine (**16**). The mp 156° was not depressed by admixture of this product with an authentic sample.

2,5-Dimethyl-2,5-diphenyldihydropyrazine (16).—2-Chloro-2-phenylpropionaldehyde (5.0 g, 0.03 mol), prepared from 2-phenylpropionaldehyde and sulfuryl chloride,[14] was dissolved in 60 ml of ethanol saturated with ammonia. After stirring for 0.5 hr at room temperature a white precipitate formed; the resulting mixture was then boiled overnight (16 hr). The residue obtained after evaporation of the ethanol was taken up in methylene chloride. This solution was washed with water, dried (K_2CO_3), and evaporated to dryness. This residue was transferred to a sublimer and pumped at 0.001 torr. A colorless oil, which was discarded, collected on the cold finger at a pot temperature of 70–95°. A white solid (2.5 g, 64%) sublimed at 100–120°; after four recrystallizations from benzene–hexane this gave **16** of mp 155–156° which exhibited an nmr spectrum ($CDCl_3$) with three singlets in the ratio 1:5:3 at δ 8.24, 7.42, and 1.63.

Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.40; H, 6.92; N, 10.68. Found: C, 82.5; H, 6.8; N, 10.9.

Conversion of 2,3-Diazido(N-phenyl)maleimide (23) into N,-N-Bis(cyanocarbonyl)aniline (24).—2,3-Diazido(N-phenyl)maleimide[16] (**23**, 2.0 g, 0.078 mol) in 60 ml of benzene was maintained at reflux in a nitrogen atmosphere for 3 hr. The solvent was removed at reduced pressure, and the brownish residue was transferred to a sublimer and heated at 70° (0.01 torr). The sublimate weighed 1.3 g (83%) and had mp 95–97°. Two recrystallization from benzene followed by a second sublimation gave **24**, mp 95–96.5°, with moderate and strong absorptions in the infrared at 4.45 and 5.81 μ, respectively.

Anal. Calcd for $C_{10}H_5N_3O_2$: C, 60.30; H, 2.53; N, 21.10. Found: C, 60.4; H, 2.7; N, 21.0.

9-Azido-9-fluorenecarbonitrile (26).—A mixture of 5.0 g (20.5 mmol) of 9-dichloromethylenefluorene (**25a**)[17] and 4 g (61 mmol) of sodium azide in 250 ml of dimethylformamide was stirred in a nitrogen atmosphere at ambient temperature overnight. This reaction mixture was diluted with *ca.* 1 l. of water and extracted five times with benzene. The benzene extracts were washed well with water, dried (Na_2SO_4), and evaporated to dryness at reduced pressure. The residue was chromatographed on 60 g of Woelm neutral alumina. Azidocyanofluorene (**26**, 1.6 g, 34%), mp 77–78°, was eluted with 1:3 benzene–hexane. The analytical sample was recrystallized from hexane and sublimed at 70° (0.001 torr) and had mp 77.5–78.5°. A carbon tetrachloride solution infrared spectrum showed the N_3 absorption at 7.74 μ. The ultraviolet spectrum in ethanol exhibited three maxima (ϵ_{231} 34,900; ϵ_{238} 33,800; ϵ_{272} 14,800) and three minima (ϵ_{217} 25,500; ϵ_{235} 30,200; ϵ_{248} 6700).

Anal. Calcd for $C_{14}H_8N_4$: C, 72.40; H, 3.44; N, 24.13. Found: C, 72.5; H, 3.8; N, 23.7.

Conversion of 9-Azido-9-fluorenecarbonitrile (26) into 10-Cyanophenanthridine (27).—A solution of 458 mg (1.92 mmol) of **26** in 2 ml of chlorobenzene was maintained at a boil in a nitrogen atmosphere for 3 hr. The reddish colored reaction solution was evaporated to dryness at reduced pressure and the residue transferred to a small sublimer. Most of the material sublimed at 140° (0.005 torr). A resublimation at 80° (0.005 torr) gave 325 mg (83%) of material having mp 138–139°. This compound had an identical infrared spectrum with that of authentic[18] 10-cyanophenanthridine (**27**) and did not depress the melting point upon mixing.

Thermolysis of Methyl Azidofumarate to 2,3-Dicarbomethoxy-2H-azirine.—Methyl azidofumarate[19] was pyrolyzed at 230° in an apparatus previously described[20] with the modification that the azide was introduced at the top of the reaction tube by suction through a very fine capillary. The pressure in the pyrolysis tube was maintained at less than 1.5 torr and the products were trapped at ice–acetone temperatures. The crude pyrolysate was Claisen distilled at 0.7 torr; the fraction collected at 70–80° was redistilled to give azirine boiling over a few degrees in an over-all yield of 35%. The azirine exhibited infrared (neat) absorption at 5.60 (C=N) and 5.73 μ (C=O). The ultraviolet spectrum (cyclohexane) consisted mainly of end absorption with

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[18] We thank Messrs. E. Hayashi and H. Ohki for a sample of 10-cyanophenanthridine [*Yakugaku Zasshi*, **81**, 1033 (1961)].

[19] V. G. Ostroverkhov and E. A. Shilov, *Ukr. Khim. Zh.*, **23**, 615 (1957).

[20] G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1966).

an inflection at 234 mμ (ε 420) tailing off to zero at about 300 mμ. The nmr (CCl_4) spectrum consisted of three sharp peaks at δ 2.85, 2.72, and 4.0 with area ratios of 1:3:3, respectively.

Anal. Calcd for $C_6H_7NO_4$: C, 45.86; H, 4.49; N, 8.92. Found: C, 45.7; H, 4.3; N, 8.7.

Registry No.—**7**, 16504-38-4; 9-(1-bromoethylidene)-fluorene, 16504-39-5; **9**, 16504-40-8; **12**, 16504-41-9; **16**, 16504-42-0; **24**, 16504-43-1; **26**, 16520-65-3; 2,3-dicarbomethoxy-2H-azirine, 16504-44-2.

Reactions of Phosphorus Compounds. XV. A General Synthesis of 2H-1-Benzopyrans

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Substituted 2H-1-benzopyrans and 3H-naphtho[2,1-*b*]pyran (IX) have been prepared from vinyltriphenylphosphonium bromide (III), substituted salicylaldehydes, or 2-hydroxy-1-naphthaldehyde, respectively.

In a previous communication in this series, 2H-1-benzopyran[1] was prepared by utilizing the vinylphosphonium salt (III) and salicylaldehyde. In addition to 2H-1-benzopyran, the following series of compounds have been synthesized: pyrrolizines,[2] carbocyclics,[3] olefins,[4a] 1,2-dihydroquinolines,[4b] and 2,5-dihydrofurans[5] from the vinylphosphonium salt (III) and suitable addenda. We now wish to report a general preparation of substituted 2H-1-benzopyrans (VI) and 3H-naphtho[2,1-*b*]pyran (IX) utilizing the vinylphosphonium salt (III) and suitable phenolic aldehydes as shown in Scheme I.

These types of compounds are of interest because of the occurrence of the benzopyran ring system in the active constituents of several plants used as insecticides[6] and natural dyes.[7] Previous preparations have been accomplished in the following manners: (a) by the intramolecular cyclization of phenyl propargyl ether;[8,9] (b) by the slow distillation of a crude mixture of 4- and 6-bromochroman in the presence of alcoholic sodium ethoxide;[10] (c) by dimethyl sulfoxide dehydration of 4-chromanol or a two-step conversion from the 4-chromanol involving a Kraft pyrolysis of 4-chromanyl acetate.[11]

In situ preparation and reaction of the sodium salts of salicylaldehyde (Id), 3-methoxy salicylaldehyde (Ia), or 2-hydroxy-1-naphthaldehyde (VIII) with the vinylphosphonium salt (III) in an acetonitrile–ether solvent system afforded 2H-1-benzopyran (VId), 8-methoxy-2H-1-benzopyran (VIa), and 3H-naphtho[2,1-*b*]pyran (IX) in 71, 57, and 14% yields respectively. 5-Chlorosalicylaldehyde (Ic) was treated in the same way (except that the solvent system used was a N,N-dimethylformamide (DMF)–ether mixture) to give 6-chloro-2H-1-benzopyran (VIc) in 29% yield. Attempted preparation of 6-nitro-1,2-benzopyran (VIb) from 5-nitrosalicylaldehyde (Ib) and the vinylphosphonium salt (III) utilizing the above procedure was unsuccessful. However, preparation and isolation of the sodium salt of 5-nitrosalicylaldehyde followed by pyrolysis with the vinylphosphonium salt (III) *in vacuo* afforded the desired benzopyran (VIb) in 27% yield.

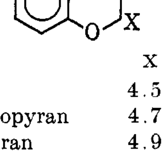
The 2H-1-benzopyrans were characterized by their physical constants, nmr spectra, and absorption in the infrared region of 1200–1260 cm^{-1} which is characteristic for the C–O stretch of aromatic ethers.[12,13]

The nuclear magnetic resonance spectra of the synthesized 2H-1-benzopyrans show patterns which are characteristic for this type of structure. The spectra can be divided into three major parts. (1) The aromatic protons appear as a multiplet. (2) The protons associated with the substituents of the aromatic ring, *i.e.*, the methyl protons of 8-methoxy-2H-1-benzopyran (VIa), exhibit a singlet centered at 3.72 ppm downfield from tetramethylsilane. (3) The protons of the pyran ring system exhibit an ABX_2 system.

The protons of the ABX_2 system exhibit the following splitting characteristics. The protons associated with the carbon α to the oxygen atom (CH_2) appear as a quadruplet ($J_{BXCH_2} = 3$ cps; $J_{AXCH_2} = 2$ cps) centered in the range of 4.37–4.96 ppm downfield from tetramethylsilane for 6-chloro-2H-1-benzopyran and 5-nitro-2H-1-benzopyran (VIb), respectively (with the others lying in between). The proton associated with the β-carbon atom appears as a pair of triplets ($J_{AB} = 10$ cps; $J_{BX} = 3$ cps) centered in the range of 5.30–5.83 ppm downfield from tetramethylsilane for 6-chloro-2H-1-benzopyran and 5-nitro-2H-1-benzopyran, respectively, at the extremes (Table I). The proton associated with the A-

Table I

Center of Nmr Bands Associated with the Pyran Ring Protons of Various 2H-1-Benzopyrans in Parts per Million from Tetramethylsilane



Compound	X	B	A
2H-1-Benzopyran	4.53	5.38	6.20
8-Methoxy-2H-1-benzopyran	4.75	5.70	6.43
6-Nitro-2H-1-benzopyran	4.96	5.83	6.42
3H-Naphtho[2-1-*b*]pyran	4.65	5.60	6.92
6-Chloro-2H-1-benzopyran	4.37	5.30	6.88

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