6b; in any event the reactions were slow relative to ring openings of **3a** and **3b.** *In pure chloroform,* **3a** *and* **3b** *do not interconvert.*

(12) Dienes **6a, 6b,** and **6c** are easily recognized in mixtures by the distinctive vinyl hydrogen signals in their NMR spectra (Figures 1 and 2). From the chemical shifts of the vinyl hydrogens of **6a, 6b, 6c,** and the *cis*- and *trans*-nitrostyrenes used as model compounds, the vinyl hydrogen signals of **6d** are expected at 6.4–6.9 and 7.5–8.0 ppm (see the discussion of NMR spectra later in this paper). Signals attributable to **6d** are not observed.

(13) Although sensitive to bases, dienes **6a** and **6b** are easily isolated and are stable during chromatography, recrystallization, etc. It thus might be expected that missing diene **6d** should have stability comparable to that of **6a** and **6b.**

(14) Attempts to generate **6d** by photoisomerization were unsuccessful. Ultraviolet irradiation of **6a** in chloroform or benzene gives **6b** and **6c.** Photolysis of **6c** in various solvents yields 2-nitro-3-phenylnaphthalene (15–30%), *trans*-2,3-diphenylacrylonitrile (5–15%), *cis*-2,3-diphenylacrylonitrile (<3%), and tar. Irradiation of solid **6c** gives tar, 2-nitro-3-phenylnaphthalene (<5%), *trans*-2,3-diphenylacrylonitrile (15–30%), and *cis*-2,3-diphenylacrylonitrile (5–10%). Cf. D. B. Miller, Abstracts of Papers, XXIII IUPAC Congress, Boston, Mass., July 1971, p 101.

(15) (a) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Am. Chem. Soc.,* **87,** 3019 (1965); (b) in the present study **4b** has been found to isomerize at least 200 times faster than **4a.**

(16) Samples of **6a** and **6c** are available for determination of their structures by crystallographic methods.

(17) Bromodiene **7b** was reduced to diene **6c** by sodium iodide in acetic acid. While this reaction has no stereochemical significance, it provides further evidence that the overall common structures of the butadienes are correct.

(18) J. A. Hirsch, *Top. Stereochem.,* **1,** 199 (1967).

(19) (a) Product **7e** forms erratically when **4a** is heated and is sometimes the major product. Since in the presence of bromine, **4a** isomerizes to **7e** at 25 °C, formation of **7e** appears to result from a bromine-catalyzed process which is independent of the thermal ring opening reactions of **4a.** (b) Bromine is a possible decomposition product of **4a** and its isomers. (c) The structure and chemistry of **7e** are under investigation.

(20) Preliminary study (see Experimental Section) indicates that isomerization of chlorocyclobutene **5a** proceeds similarly to that of its structural analogue, bromocyclobutene **4a.** Lack of sample prevented detailed study of **5a.**

(21) Limiting estimates as to the proportion of **7a** in equilibrium with **4a** and the rate of cyclization of **7a** give rate constants for ring opening of **4a** between 0.015×10^{-6} and 0.33×10^{-6} s^{-1}; see Experimental Section for details.

(22) (a) A. A. Dudinskaya, G. A. Shvekhgeimer, S. S. Novikov, and V. I. Slovetskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.,* 168 (1961); *Chem. Abstr.,* **55,** 18559 (1961); (b) A. L. Bluhm and J. Weinstein, *J. Am. Chem. Soc.,* **87,** 5511 (1965); (c) J. A. Sousa, J. Weinstein, and A. L. Bluhm, *J. Org. Chem.,* **34,** 3320 (1969).

(23) H. L. Goebel and H. H. Wenzke, *J. Am. Chem. Soc.,* **60,** 697 (1938); G. Drefahl and G. Heublein, *Chem. Ber.,* **93,** 497 (1960); V. N. Vasil'eva, V. V. Perekalin, and V. G. Vasil'eva, *J. Gen. Chem. USSR (Engl. Transl.),* **31,** 2027, 2031 (1960).

(24) (a) A formula given in *Chem. Abstr.,* **55,** 14580 (1961), as $C_6H_5C(R')=CHNO_2$ (R' = methyl and other groups) should be $C_6H_5CH=C(R')NO_2$; (b) K. A. Oglobin and V. P. Semenov, *Zh. Obshch. Khim.,* **29,** 2660 (1959) [*Chem. Abstr.,* **54,** 8679 (1960)], report an **11a** with n^{20}D 1.5803; (c) C. A. Burkhard and J. F. Brown, Jr., U.S. Patent 2 867 669 (Jan 6, 1959), describe a mixture, n^{20}D 1.5831, containing 60% **11a** and 40% **11c.**

(25) W. K. Siefert, *J. Org. Chem.,* **28,** 125 (1963).

(26) Solid **9a** is photodimerized by sunlight to 1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane.[9]

(27) Nitro olefins **12b** and **13b** are isomerized more rapidly than is **10b** by triethylamine.

(28) (a) In carbon tetrachloride at 25 °C, the equilibrium proportions of **11a, 11b,** and **11c** are 73, 2, and 25%, respectively. (b) Comparison of indices of refraction suggests that the nitromethylstyrenes of ref 24b and 24c are mixtures of isomers. Cf. values of n^{20}D for **11a, 11b,** and **11c** reported in the Experimental Section of the present paper.

(29) (a) H. Shechter and J. W. Shepherd, *J. Am. Chem. Soc.,* **76,** 3617 (1954); (b) L. V. Phillips and D. M. Coyne, *J. Org. Chem.,* **29,** 1937 (1964); (c) see also L. Bouveault and A. Wahl, *Bull. Soc. Chim. Fr.,* **25,** 808 (1901); H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.,* 604 (1934); (d) M. J. S. Dewar, *Discuss. Faraday Soc.,* **2,** 261 (1947).

(30) S. Bank, A. Schriesheim, and C. A. Rowe, Jr. [*J. Am. Chem. Soc.,* **87,** 3244 (1965)], S. Bank [*ibid.,* **87,** 3245 (1965)], and R. Hoffmann and R. A. Olofson [*ibid.,* **88,** 943 (1966)] have discussed allylic anions which are thermodynamically more stable in cis than in trans forms.

(31) (a) Similar correlations have been reported for α,β-dialkylstyrenes,[31b] β-bromo-α-methylstyrenes,[31c] β-bromostyrenes,[31d] and β-acetoxystyrenes.[31d] The changes in chemical shift as a result of cis–trans isomerism in β-nitrostyrene are considerably larger, however, presumably because of the magnetic anisotropy of the nitro group. (b) M. Barbieux, N. Defay, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belg.,* **73,** 716 (1964). (c) D. R. Davis and J. D. Roberts, *J. Am. Chem. Soc.,* **84,** 2252 (1962). (d) D. T. Witiak and B. B. Chaudhari, *J. Org. Chem.,* **30,** 1467 (1965).

(32) (a) E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.,* 1104 (1947); (b) M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.,* **77,** 5696 (1955).

(33) We thank F. M. Evans and B. J. Taylor, Continental Oil Co., Ponca City, Okla., for determining some of the uv spectra and L. D. Stietzel and H. C. Barrett, Stanford Research Institute, Menlo Park, Calif., for recording many of the NMR spectra.

(34) D. E. Worrall, *Org. Synth.,* **9,** 66 (1929).

(35) H. B. Hass, A. G. Susie, and R. L. Heider, *J. Org. Chem.,* **15,** 8 (1950).

(36) W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.,* **73,** 4664 (1951).

Carbenic Processes in Decomposition of Spiro[fluorene-9,3′-indazole]. A Simple Route to the Fluoradene System

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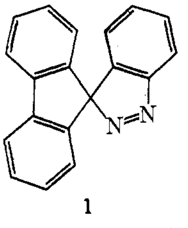
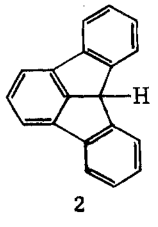
Spiro[fluorene-9,3′-indazole] (1), obtained along with 9-fluorenyl anthranilate (6) by aprotic diazotization of anthranilic acid in the presence of 9-diazofluorene (3), thermolyzes to fluoradene (2), 12,12′-bifluoradene (8), and 9-phenylfluorene (9). Thermolysis and photolysis of 1 in solution are interpretable on the basis of formation of triplet 2-(9-fluorenylidene)-3,5-cyclohexadienylidene (13), isomerization of 13 to 2, and hydrogen abstraction by 13 to yield the fluoradenyl (15) and the 9-phenylfluorenyl (16) radicals and their subsequent products. Irradiation of 1 in 2-methyltetrahydrofuran at 77 °C gives intense ESR absorption for 13. Decomposition of 1 occurs photolytically in *N*-phenylmaleimide with loss of nitrogen to form the adduct **20**, $C_{29}H_{19}NO_2$. In benzene 1 photolyzes in the presence of oxygen to 2 and 8 along with 9,9-diphenylfluorene (23), 9-phenylfluorenyl peroxide (25), and biphenyl (28). Photolysis of 1 in ethyl ether and exposure of the reaction mixture to oxygen results in near-quantitative formation of 25.

Synthesis of 3-substituted 3*H*-indazoles and determination of the products and the mechanisms of their isomerization and decomposition are being studied in this laboratory.[1,2] We now describe the preparation and the thermolysis and photolysis reactions of spiro[fluorene-9,3′-indazole] (1). Decomposition of 1 is significant in that its intramolecular and intermolecular reactions take place by triplet carbenic processes. Thermolysis and photolysis of 1 are also of value in that the interesting hydrocarbon, fluoradene (2), is formed efficiently.[3]



1



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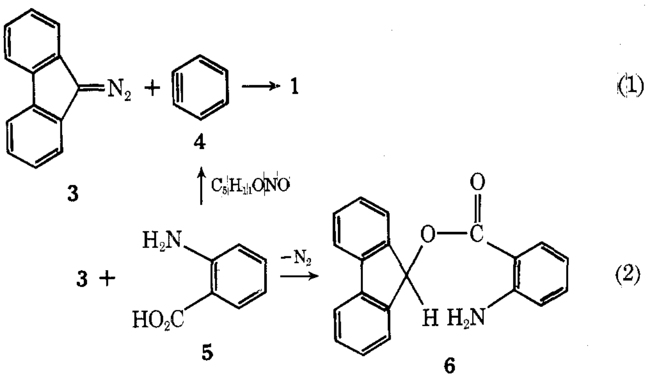
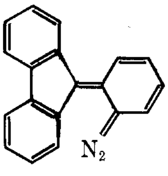
Spiroindazole 1 is prepared in 70–80% yields by cycloaddition (eq 1) of 9-diazofluorene (3) to benzyne (4) as gener-



(1)

(2)

ated by aprotic diazotization of anthranilic acid (**5**).[4] Satisfactory yields of **1** are obtained when **5** is added very slowly, with repeated interruption, to isoamyl nitrite and **3** in tetrahydrofuran at 45 °C; a by-product arising from reaction of **3** with **5** is 9-fluorenyl anthranilate (**6**, eq 2). Indazole **1** is a light yellow solid which melts at 165–167 °C with vigorous evolution of nitrogen. Its NMR spectrum indicates only aromatic protons (a multiplet centered at τ 2.8); its ir properties reveal that a diazo group is absent and thus rule out diazo compound **7** as the structure of that assigned



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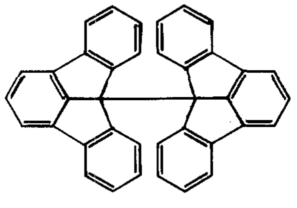
as **1**. The ir absorptions at 720–760 cm^{-1} for out-of-plane deformation of aromatic protons are consistent with that for the four adjacent hydrogens in the aryl moieties in **1**.

Thermolysis of **1** results in formation of fluoradene (**2**), 12,12′-bifluoradene[5] (**8**), and 9-phenylfluorene (**9**); benzocyclopropene **10**[6] was not detected. The synthesis of **2** is of



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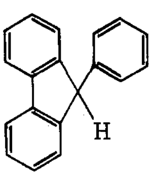

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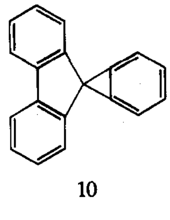

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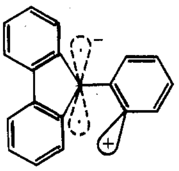
value in that it is a relatively simple entry to fluoradenyl systems;[3] **2** is an impressive hydrocarbon acid (pK_a′ = 11 ± 0.05 in 20% aqueous methanol) and a convenient source of the fluoradenyl carbanion.[3] The products of decomposition of **1** are readily separated by thin layer and column chromatographic techniques and are differentiated by their ir and NMR properties. The ir spectrum of **2** includes sharp absorption at 825 cm^{-1} assignable to the out-of-plane deformation of aromatic C–H for three adjacent protons; the band appears at 800 cm^{-1} in **8** and is missing in **9**. Strong absorption at 700 cm^{-1} in **9** is indicative of its monosubstituted phenyl group. The tertiary hydrogen of **9** is revealed by a single NMR resonance peak at τ 5.1 in carbon tetrachloride; for **2** the resonance occurs at τ 4.95. The shift to lower field in **2** indicates that its tertiary CH is more nearly in the plane of its phenyl groups and thus is more deshielded by diamagnetic ring currents than is the methyne hydrogen in **9**.

Conversion of **1** to **2** is greatly affected by the decomposition method. Solid **1**, upon rapid (5 min) heating to 160 °C, gives **2** (40%) along with near-equivalent quantities of **8** (19%) and **9** (22%); upon heating **1** slowly to 160 °C, the yield of **2** is diminished (10%) and **8** (32%) and **9** (34%) are the principal products. Fluoradene (**2**) is thus an initial product of bulk thermolysis of **1** but is partly consumed by hydrogen transfer processes and conversion to **8**. These conclusions are substantiated by the results of thermolysis of **1** in solution in various solvents.

Thus rapid addition of solid **1** to refluxing *o*-dichlorobenzene (178 °C) gives **2** as the major product (70–80%) along with small quantities (<2%) of **8** and **9**. When the decomposition is effected by addition of **1** to refluxing decalin (162–164 °C), **8** (39%) is the principal product along with **2** (9%) and **9** (14%). Thermolysis of **1** in an inert solvent such as *o*-dichlorobenzene minimizes the formation of products resulting from hydrogen transfer from solvent and is the method of choice for synthesis of **2**. Slow or rapid addition of **1** to refluxing *o*-dichlorobenzene does not affect the yield of **2**; apparently in dilute solution hydrogen transfer from **2** resulting in **8** and **9** cannot compete effectively with the conversion of **1** to **2**.

The mechanisms of conversion of **1** to **2**, **8**, and **9** are of certain interest. Intermediates such as **7** and **10** may be actually involved upon decomposition of **1**; however there is no concrete evidence at present relative to these possibilities.[7] Loss of nitrogen from **1** and geometric change can give the divalent intermediates represented as **11–13**. Dipolar singlets **11** and **12** differ in the electron distribution in their π and σ atomic orbitals;[8] **13** is a diradical. Thermolysis of **1** might initially give singlets such as **11–12** or their prior rotamers. The conversions of **1** to **2**, **8**, and **9** are most readily interpreted, however, on the basis of the eventual intermediacy of **13**. Conversion of **13** to **7** would thus involve diradical addition at the 1 position of the fluorene moiety and subsequent isomerization of **14** (eq 3). A result



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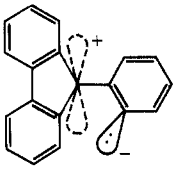

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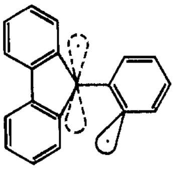
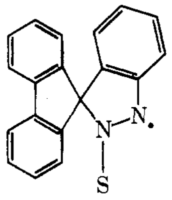


from **2** or/and **14** to **13** to form fluoradenyl (**15**) and 9-phenylfluorenyl (**16**) radicals. Dimerization of **15** yields **8**; abstraction of hydrogen from **2**, **8**, or/and **14** by **16** results in **9** (eq 5). Heating **1** slowly to 160 °C increases the conver-

$$2\,\mathbf{15} \longrightarrow \mathbf{8}{:}\,\mathbf{16} + \mathbf{2}\ \text{and/or}\ \mathbf{14} \longrightarrow \mathbf{9} \qquad (5)$$

sions to **8** and **9** because of the increased opportunity of hydrogen transfer from **2** and **14**. Similarly, decomposition of **1** in decalin results in hydrogen transfer from the solvent to **15** and **16** and thus enhanced formation of **8** and **9**.

Photolysis of **1** also gives information that triplet **13** is generated. The ESR spectrum of **13** obtained upon irradiation of **1** in a matrix of 2-methyltetrahydrofuran at 77 K reveals intense absorption at 3210 G (g = 2.0022) and poorly resolved satellite bands, all split into doublets.[9] At half-field (1618.4 G, A_M = 2) absorption at lower intensity is observed. Irradiation of **1** at 295 K in 2-methylfuran yields an ESR spectrum consisting of seven lines with an intensity ratio of 1:1:2:1:2:1:1 with each line further split into a triplet. The ESR signal persists for over 1 h. The spectrum is consistent for electron interaction with two nitrogens (splitting constants are 11.75 and 6.7 G) and two equivalent protons (1.8 G). Radical **17**, as formed by homolytic attack at nitrogen 2 of undecomposed **1**, conforms to the observed spectrum. Radical **17** is structurally related to the stable 1,1-diphenylpicrylhydrazyl (**18**)[10] and the 1,2-diphenyl-1-(2-phenyl-2-propyl)hydrazyl (**19**)[11] radicals. The structure of the radical moiety (S) in **17** is not known.



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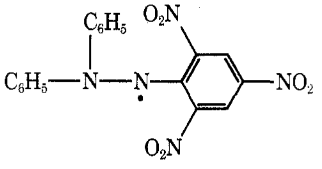

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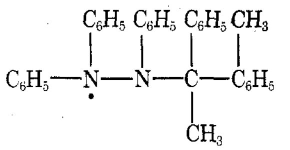
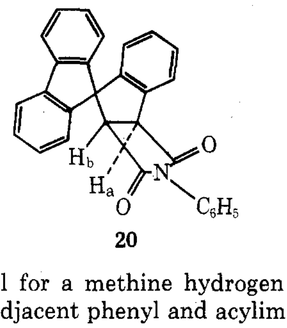


$$\mathrm{C_6H_5{-}\underset{\bullet}{\overset{C_6H_5}{N}}{-}\overset{C_6H_5}{N}{-}\underset{CH_3}{\overset{C_6H_5\ CH_3}{C}}{-}C_6H_5}$$

19

Photochemical transformations of **2** also provide insight as to the nature of the intermediates produced. Irradiation of **2** in the presence of excess N-phenylmaleimide at 0 °C yields an adduct $C_{29}H_{19}NO_2$ presumably derived by capture of **13**. The structure of the product is assigned as **20** on the basis of its elementary analysis, molecular weight, origins, and its ir and NMR spectra. The ir spectrum of the adduct does not exhibit absorption bands for a fluoradene derivative or an unsymmetrical olefin. The NMR spectrum has absorption bands in only three regions: τ 2.3 (m, 16 H), 7.85 (s, 1 H), and 8.60 (s, 1 H). The band at τ 7.85 (**20**, proton a) is normal for a methine hydrogen with slight deshielding from adjacent phenyl and acylimide groups. Proton b (**20**, τ 8.60) is located below the plane of the fluorene ring and is expected to be shielded by the diamagnetic ring current of the aromatic system.



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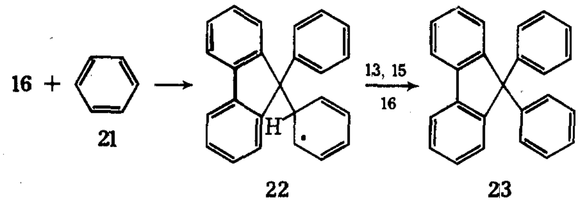
Photolysis of **1** in solution yields **2**, **8**, and **9** along with products derived from reactions with solvents and added oxygen. Thus irradiation of **1** in benzene (**21**) gives **2** (12%), **8** (21%), 9,9-diphenylfluorene (**23**, 15%), 9-phenylfluorenyl peroxide (**25**, 43%), and biphenyl (**28**). Formation of these products indicates that major aspects of photolytic and thermal decompositon of **1** are similar and presumably involve **13** as an initial common intermediate. Homolytic addition of **16** to **21** and hydrogen transfer to radicals such as **13**, **15**, and **16** account for formation of **23** (eq 6). Capture of oxygen by **16** leads to **25** (eq 7). A highly energetic intermediate generated by photolysis of **1** presumably abstracts hydrogen from **21** to produce phenyl radicals (**26**); **28** is apparently formed (eq 8) by addition of **26** to **21** and removal of hydrogen from **27** by various radicals in the reaction environment.



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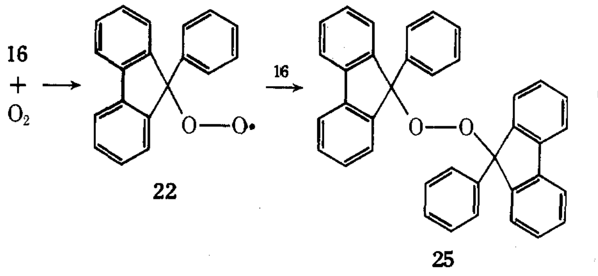

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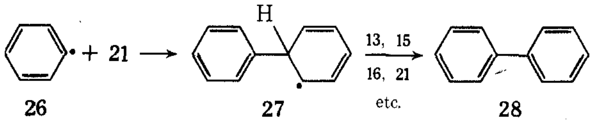

(8)

Photolysis of **1** in solvents which function as effective hydrogen atom donors enhances partitioning of **13** to **16** and its subsequent products. Thus irradiation of **1** in toluene at 65 °C yields **9** (51%) along with **2** (9%) and **8** (8%); of particular note is that, upon photolysis of **1** in ethyl ether at −95 °C and subsequent exposure of the reaction mixture to oxygen, **25** is formed in ~100% yield.

The chemistry of various 3,3-disubstituted 3H-indazoles will be described in subsequent publications from this laboratory.

Experimental Section

Spiro[fluorene-9,3′-indazole] (1). A solution of anthranilic acid (**5**, 15.10 g, 0.11 mol) in tetrahydrofuran (400 ml) was added in 25 h to a stirred solution of 9-diazofluorene (**3**, 20.00 g, 0.104 mol) and isoamyl nitrite (14.05 g, 0.12 mol) in tetrahydrofuran (25 ml) at 43.5–46.5 °C. Gas evolution totaled 3750 ml (81%). The reaction mixture was evaporated in vacuo to a viscous red oil which was dissolved in methylene chloride and washed with water. After the methylene chloride solution was dried over magnesium sulfate, the solvent was removed in vacuo and the residue was recrystallized from warm ligroin and benzene to yield pale yellow prisms (16.81 g, 60%) of **1**, mp 163–166 °C dec. Recrystallization from cyclohexane afforded the analytical sample, mp 166–167 °C dec.

Anal. Calcd for $C_{19}H_{12}N_2$: C, 85.05; H, 4.51; N, 10.44. Found: C, 85.14; H, 4.42; N, 10.38.

In various preparations of **1**, 9-fluorenyl anthranilate (**6**) was obtained from reaction of **3** and **5**.

Reaction of Anthranilic Acid (5) with 9-Diazofluorene (3). A solution of **5** (1.37 g, 0.01 mol) and **3** (1.92 g, 0.01 mol) in methylene chloride (70 ml) was refluxed for 11 h. The solution was washed with 5% aqueous sodium hydroxide, and the methylene chloride layer was dried and evaporated. The residue, on recrystallization from cyclohexane, yielded highly fibrous white needles of 9-fluorenyl anthranilate (**6**, 1.10 g, 37%, mp 100–102 °C).

The infrared spectrum of **6** displays absorption bands at 3450 and 3300 (N–H stretching of $-NH_2$), 3050 (aromatic C–H stretching), 2900 (aliphatic C–H stretching), 1670 (C=O stretching), 1240 and 1100 (C–O–C stretching of esters), 745 (multiplet, out-of-plane C–H bending of 1,2-disubstituted benzenes), and 700 cm^{-1} (perhaps out-of-plane bending of NH_2). Mol wt, calcd, 301; found, 294.[12]

Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.01; N, 4.65. Found: C, 79.24; H, 5.15; N, 4.66.

Bulk Thermolysis of Spiro[fluorene-9,3′-indazole] (1). A. Slowly Heated to 161 °C. A cylinder containing finely ground **1** (2.00 g, 7.46 mmol) was connected to a gas buret and flushed with nitrogen for 1 h. The cylinder was lowered into an air bath which was heated from 25 to 161 °C in 2 h. At 155 °C, gas evolution was detectable and at 161 °C, the theoretical volume of nitrogen was evolved vigorously. The reaction mixture was stirred with hot benzene and, after filtration, yielded 12,12′-bifluoradene (**8**, 0.26 g). The filtrate was evaporated to dryness, dissolved in ligroin (bp 60–90°C) containing a minimum amount of benzene, and then chromatographed on silica gel (40 g). Elution with ligroin–benzene (4:1) produced a mixture (0.77 g) of 9-phenylfluorene (**9**, 34% yield) and fluoradene (**2**, 10% yield).[13] Additional **8** (0.18 g, 32% total yield) was obtained by eluting the column with ligroin–benzene (3:2). Continued elution with (1) ligroin–benzene (2:3) gave a purple residue (0.12 g, 13%, mp 210 °C dec) that was unidentified and (2) benzene allowed recovery of **1** (0.01 g).

Fractionation of the chromatographic eluents was greatly aided by concurrent thin layer chromatographic analysis of the fractions. A sample of the eluent placed on silica gel coated glass plates was developed with ligroin–benzene (2:1). When sprayed with sulfuric acid, **2** and **9** appear together at R_f 0.65 as maroon spots, **8** is at R_f 0.42 as a blue-gray spot, and **1** is found at R_f 0.10 as a brown spot.

The physical properties of **2** follow: mp 132–132.5 °C (lit. mp 130 °C);[3b] uv λ_{max} 220 nm (ϵ 42.6 × 10^3) and 275 (30.6 × 10^3) [lit. 276 nm (ϵ 26.6 × 10^3)];[3b] ir 825 cm^{-1}; and NMR τ 7.1–7.8 (aromatic m, 12 H) and 4.95 (s, 1 H). Mol wt, calcd, 240; found, 248.[12]

Anal. Calcd for $C_{19}H_{12}$: C, 94.93; H, 5.03. Found: C, 95.30; H, 4.91.

12,12′-Bifluoradene (**8**), mp 303–305 °C dec (lit. mp 306–307 °C dec),[3b] exhibits uv λ_{max} 285 nm (ϵ 26.6 × 10^3) [lit. 285 nm (ϵ 40 × 10^3)[3b] and 226 (60 × 10^3)] [lit. 225 (100 × 10^3).[3b] The poor agreement with the literature values for ϵ is probably a result of the extreme insolubility of **8**. The ir absorption of **8** reveals a sharp band at 800 cm^{-1}; its NMR indicates only aromatic protons.

Anal. Calcd for $C_{38}H_{22}$: C, 95.37; H, 4.63. Found: C, 95.45; H, 4.56.

The identification of **9** (mp 145 °C) was effected by mixture melting point and comparison of its ir and NMR spectra with those of an authentic sample.

B. Rapidly Heated to 200 °C. Finely ground **1** (1.073 g, 4.01 mol) was placed in a test tube connected to a cold trap and a vacuum pump. A slow stream of nitrogen was passed through the tube maintained at 78 mmHg. The tube was lowered into a sand bath at 200 °C. Within a few minutes a vigorous reaction occurred which was accompanied by frothing of the mixture. After 15 min the mixture was cooled, stirred with hot benzene, and filtered to give **8** (179 mg, 19%). Chromatography of the filtrate on silica gel and elution with ligroin–benzene mixtures produced **9** (200 mg, 22%), **2** (330 mg, 40%), an unidentified purple residue (120 mg, 13%), and recovered **1** (158 mg).

Solution Thermolysis of Spiro[fluorene-9,3′-indazole] (1). A. Rapid Addition to *o*-Dichlorobenzene. A solution of **1** (1.1515 g, 4.32 mmol) in *o*-dichlorobenzene (10 ml) was rapidly injected with a hypodermic syringe through a serum cap into refluxing (178 °C) *o*-dichlorobenzene (250 ml). The theoretical volume of nitrogen was evolved in 25 min. The solution was evaporated to dryness in vacuo. Recrystallization from ligroin yielded a trace of **8**, pure **2** (0.599 g, 58%), and a mixture of **2** and **9** (0.019 g, 1.8%).

B. Slow Addition to *o*-Dichlorobenzene. A solution of **1** (2.010 g, 7.50 mmol) in *o*-dichlorobenzene was added in 10 min to refluxing *o*-dichlorobenzene (250 ml). The theoretical volume of nitrogen was evolved in 44 min. After the reaction mixture had been evaporated to dryness in vacuo, the residue was recrystallized from cyclohexane to give **8** (5.1 mg, 0.3%), pure **2** (1.28 g, 53%), and a mixture (0.27 g, 13%) which was primarily **2** (based on ir analysis).

C. Decalin. Solid **1** (1.3270 g, 4.95 mmol) was rapidly added to refluxing decalin (100 ml, 163 °C). The theoretical volume of nitrogen was evolved in 1 h. The solution was evaporated to dryness in vacuo and the residue stirred with hot ligroin. Filtration yielded **8** (0.342 g, 38.9%,). Fractional crystallization of the residue gave a mixture of **2** (9%) and **9** (14%) (as determined by NMR) and a tacky oil (0.34 g, 38%) that resisted crystallization.

Solution Photolysis of Spiro[fluorene-9,3′-indazole] (1). A. In Concentrated Benzene Solution at 29 °C. A solution of **1** (1.00 g, 3.73 mmol) in benzene (40 ml), was added to a Pyrex tube connected to a condenser and gas buret. The solution was purged with dry nitrogen for 1 h followed by irradiation at 29 °C for 20 h with a 100-Watt high pressure mercury arc lamp (Hanovia 616A). White crystals deposited during irradiation; the theoretical volume of nitrogen was evolved.

Filtration of the reaction mixture yielded **8** (0.35 g). Chromatography of the filtrate on alumina (Woelm, neutral grade) and elution with ligroin–benzene (1:1) allowed isolation of 9,9-diphenylfluorene (**23**, 0.20 g, 17%) identified by its analysis and comparison with literature properties:[14] ir 740 (complex multiplet) and 700 cm^{-1}; NMR, complex aromatic multiplet.

Anal. Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.67; H, 5.86.

Continued elution with ligroin–benzene resulted in additional **8** (0.58 g, 65% total yield).

B. In Dilute Benzene Solution at 14 °C. A stirred solution of **1** (2.00 g, 7.47 mmol) in benzene (800 ml) was purged with nitrogen and then irradiated in Pyrex at 12–16 °C with an internally mounted 450-W high-pressure mercury arc lamp (Hanovia 679A) for 45 min. The solution was concentrated in vacuo and chromatographed on silica gel to give **2** (0.21 g, 12%; by elution with ligroin), **23** (0.36 g, 15%; by elution with 4:1 ligroin–benzene), 9-phenylfluorenyl peroxide (**25**; 0.38 g, 21%; by elution with 3:1 benzene–ether), and **8** (0.38 g, 21%; by elution with 3:1 benzene–ether).

Peroxide **25**, mp 193–194 °C in sealed capillary (lit. mp 193–194 °C),[15] exhibits only an aromatic NMR multiplet. Its ir spectrum displays strong bands at 1010, 750 (complex multiplet), and 695 cm^{-1}

Anal. Calcd for $C_{38}H_{26}O_2$: C, 88.69; H, 5.09. Found: C, 89.12; H, 5.04.

In a separate experiment, **1** (1.50 g, 5.60 mmol) in benzene (600 ml) was irradiated for 60 min at 14–18 °C. The solution was evaporated to dryness and chloroform (10 ml) was added. Gas chromatography on Apiezon L (23%) on Chromosorb P revealed the presence of biphenyl (**28**, 0.002 g, 0.23%).

C. In Dilute Toluene. A stirred solution of **1** (1.99 g, 7.45 mmol) in toluene (700 ml) in Pyrex was purged with nitrogen for 1 h followed by irradiation at 65 °C with an internally mounted 450-W high-pressure mercury arc lamp (Hanovia 679A) for 35 min. The residue remaining after solvent removal in vacuo was stirred with hot benzene and filtered to give **8** (146 mg, 8%). Fractional crystallization of the filtrate with added ligroin produced **2** (136 mg, 9%) and **8** (891 mg, 51%).

D. In Dilute Ethyl Ether. A solution of **1** (2.00 g, 7.47 mmol) in ethyl ether (638 ml) was purged with dry nitrogen for 0.5 h followed by irradiation in Pyrex for 40 min at −92 to −96 °C with a 450-W high-pressure mercury arc lamp (Hanovia 679A).

The residue remaining after evaporation of the solvent in vacuo was dissolved in benzene and the red benzene solution was chromatographed on Woelm alumina (acid activity I). Elution with ligroin containing increasing amounts of benzene yielded only **25** (>1.85 g, >98%).

E. In Benzene with *N*-Phenylmaleimide. A solution of **1** (1.63 g, 6.08 mmol) and *N*-phenylmaleimide (2.00 g, 11.5 mmol) in benzene (400 ml)–*o*-dichlorobenzene (400 ml) was irradiated in Pyrex at 2 to −5 °C for 45 min with a 450-W high-pressure mercury arc lamp (Hanovia 679A). The solution was evaporated to dryness and the residue extracted with hot water (600 ml); a portion of the *N*-phenylmaleimide (1.62 g) was recovered. The residue, after extraction, was dissolved in benzene (a small amount of **8** was removed by filtration) and chromatographed on silica gel. Elution with ligroin–benzene (2:1) gave a trace amount of **23**; elution with benzene–chloroform (5:1) produced a mixture of **1** and the adduct **20** which could not be separated without great loss. An analytical sample of **20**, mp 205–205.5 °C, was obtained by repeated crystallization from cyclohexane.

Anal. Calcd for $C_{29}H_{19}NO_2$: C, 84.24; H, 4.63; N, 3.38; mol wt, 413. Found: C, 84.64; H, 5.13; N, 3.25; mol wt, 439.

Electron Spin Resonance Spectra. The ESR spectra were obtained with a Varian V 4500 spectrophotometer operated at 10 FC modulation and a rf energy of 8996 MHz. The magnetic field was scanned from 1000 to 10 000 G.

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Registry No.—**1**, 161-36-4; **2**, 205-94-7; **3**, 832-80-4; **5**, 118-92-3; **6**, 57762-01-3; **8**, 57762-02-4; **9**, 789-24-2; **20**, 57762-03-5; **23**, 20302-14-1; **25**, 35377-95-8; *o*-dichlorobenzene, 95-50-1; decalin, 91-17-8; *N*-phenylmaleimide, 941-69-5.

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Diels–Alder Reactions Involving Heterocyclic Dienophiles. Synthesis of Substituted Hydroquinazolines and 1,3-Diazaspiro[4.5]decadienes

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A direct synthetic route to substituted 2-aminohydroquinazolines **6** (**b**, **c** and/or **d**, **f**, and **g**) and 2-amino-1,3-diazaspiro[4.5]-deca-1,7-dien-4-ones **5** (**b**, **c** and/or **d**, **e**, and **f**) is described. The key step is a Diels–Alder reaction between heterocyclic dienophiles **2** and **4** and a series of 1,3-dienes. Attempts to prepare **6b** from the readily available methyl orotate-1,3-butadiene adduct **7** resulted in a rearrangement, producing spiral compounds **5a** and **9**. The structure of the hydrobromide salt **12** of amine **5a** was determined by x-ray crystallographic analysis, confirming the structure assignments in the entire series.

Our interest in the Diels–Alder reaction involving hydropyrimidine dienophiles stems from the possibility of utilizing the resulting hydroquinazoline adducts for the synthesis of biologically interesting analogues of the powerful nerve poison tetrodotoxin.[2] Carbomethoxyisocytosine **4** (Chart I) is an especially attractive candidate for the Diels–Alder reaction and, based on the original work of Ruhemann and Stapleton[3] in the ethyl ester series, appeared to be readily prepared by acetylation of the product, mp >345 °C, obtained by the condensation of dimethyl acetylenedicarboxylate with guanidine carbonate in methanol containing sodium methoxide.

Recently, Katner and Ziege[4] assembled uv evidence and some chemical evidence which seemed to require that the Ruhemann and Stapleton condensation afforded imidazoline **1** rather than isocytosine **3**. Katner and Ziege further showed that the original condensation product could be isomerized by hot sodium hydroxide followed by reesterification to a compound, mp 288–291 °C, to which they assigned the structure **3**. In this present paper we illustrate a new synthetic route to substituted 2-aminohydroquinazolines utilizing acetylated pyrimidone **4** as a dienophile. During the course of this work rearrangements were encountered which eventually required an x-ray crystallographic analysis in order to confirm the structure assignments in this entire series.

Results and Discussion

Acetylation of Katner and Ziege's mp 288–291 °C material **3** (correct structure assignment, see below) afforded acetyl derivative **4**.[4] Reaction of **4** with excess 1,3-butadiene[5] in THF at 195 °C for 2 days afforded hydroquinazoline **6b** in 9% yield as a 65:35 mixture of isomers at C-10. These substances were clearly (by NMR) isomeric to the butadiene adduct **5b**[2,5] derived in 72% yield from imidazoline **2**. Ammonium hydroxide–MeOH hydrolysis to crystalline **6a** followed by reacety-