Synthesis and Photochemical Decomposition of Some Substituted 1,2-, 1,2,3-, and 1,2,4-Azafulvenes

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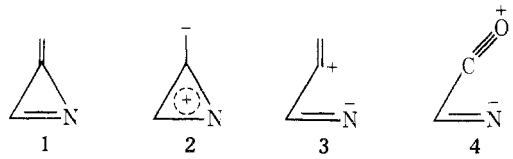
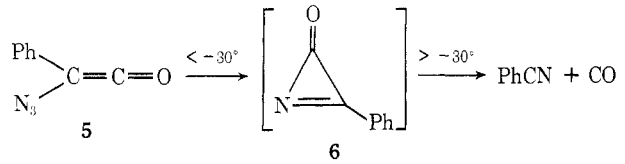
A series of phenylpyrazole and -triazole diphenylcarbinols have been converted to the hydrochloride salts of the carbinyl chlorides and thence to the corresponding azafulvenes by dehydrohalogenation with triethylamine at −78°. Irradiation of the triazafulvenes at this temperature gave a mixture of isolable products which implicate azatriafulvene and azete as possible unstable precursors. The latter intermediate may also be involved in the photochemical decomposition of triphenyltriazine, which was also examined. The diazafulvenes prepared proved isolable but photochemically inert.

Continuation of our studies on the potential synthesis of small-ring heterocycles by photochemical expulsion of a stable fragment such as nitrogen from a suitable larger-membered ring precursor has led us to examine the photochemistry of some substituted di- and triazafulvenes.[1] From initial mechanistic speculation one could envision the fragmentation of heterofulvenes with a contiguous triaza function as an entry into the class of theoretically interesting azatrifulvenes, **1**. Such systems would suffer a destabilizing electrostatic effect from the heterosubstitution in the charge-separated resonance contributor, **2**, but be more stable toward thermal fragmentation if the required (orbital symmetry) intermediate, **3**, is considered relative to an azirinone-derived model (**4**).



1 **2** **3** **4**

In fact, a synthetic effort directed toward the synthesis of **6** *via* the azidoketene **5** gave only benzonitrile and carbon monoxide.[2] Presently, we wish to describe the details



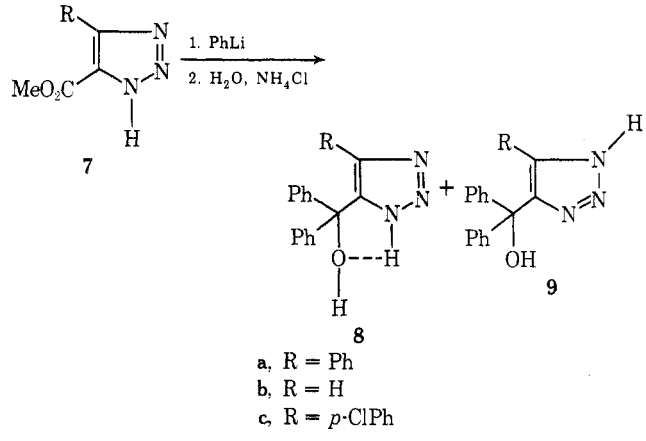
5 **6**

of the synthesis and photochemical reactions of some 1,2-, 1,2,3-, and 1,2,4-azafulvenes.

Results and Discussion

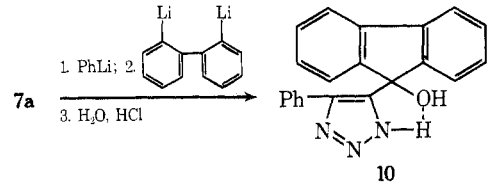
Recent synthetic efforts in the area of heterofulvenes have been successful in the construction of 1,4-diazafulvenes *via* dehydrohalogenation[3] of substituted 2-chloromethylimidazolium chlorides or oxidation[4] of *p*-4,5-diphenyl-2-imidazolylphenol and azafulvenes by analogous reactions with suitable pyrrole precursors.[5] The azafulvenes prepared in this study were derived from the appropriate chlorodiphenylmethylazole hydrochloride salts by deprotonation and dehydrohalogenation with triethylamine.

Synthesis of 1,2,3- and 1,2,4-Triazafulvenes. The addition of phenyllithium to methyl 4-phenyl-1,2,3-triazole-5-carboxylate[6] (**7a**), ethyl 1,2,3-triazole-5-carboxylate[7] (**7b**), or methyl 4-(*p*-chlorophenyl)-1,2,3-triazole-5-carboxylate (**7c**) followed by hydrolysis gave the carbinols **8a–c** and **9a**. The precursor **7a** was prepared by the addition of sodium azide to methyl *p*-chlorophenylpropiolate[8] in DMF at 30°. The fluorenol derivative **10** resulted from the action of *o,o'*-dilithiobiphenyl[9] on the lithium salt of **7a** in



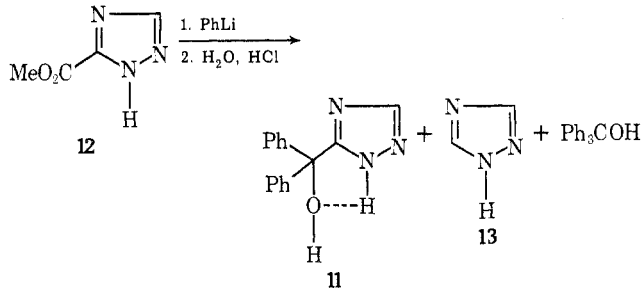
7 **8** **9**

a, R = Ph
b, R = H
c, R = *p*-ClPh



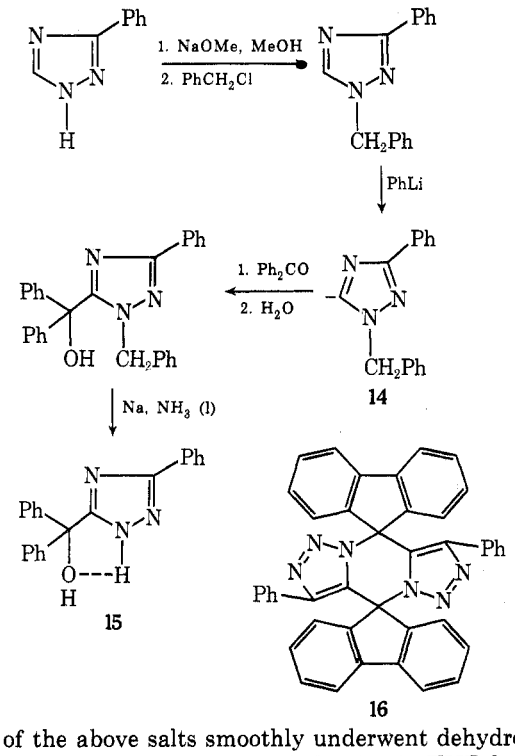
10

ether solution. In the 1,2,4-triazole system, the synthesis of carbinol **11** *via* addition of phenyllithium to methyl 1,2,4-triazole-3-carboxylate[10] (**12**) was complicated by a



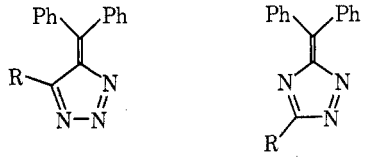
12 **11** **13**

competing retro-aldol reaction which gave **13** and triphenylcarbinol. The corresponding 3-phenyl derivative, **15**, resulted from the addition of the 1-benzyl-3-phenyl-1,2,4-triazolyl anion,[11] **14**, to benzophenone followed by reductive debenzylation. The requisite chlorodiphenylmethylazole hydrochloride salts were obtained in high yield from treatment of carbinols **8a**, **8b**, **8c**, **11**, and **15** with thionyl chloride in benzene at 30°. On the other hand, the reaction of **10** with this reagent gave a dimer ($C_{42}H_{26}N_6$) whose spectral display and observed facile acid-catalyzed hydrolysis to **10** suggests a structural assignment of **16**. It is not known if such a transformation involves an antiaromatic azafulvalene intermediate, although a similar dehydration–dimerization reaction product has been reported in the case of α,α-diphenyltetrazole-5-methanol.[12]



14 15 16

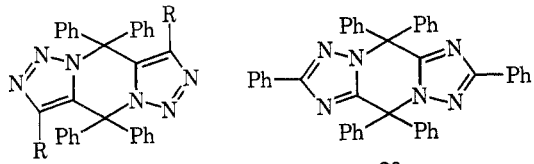
All of the above salts smoothly underwent dehydrohalogenation in the presence of triethylamine in THF–benzene (1:1) at −78° to afford solutions of the fulvenes **17** and **18**. However, the color of solutions of **17a** and **18a** at this temperature began to fade rapidly and further exploration of the chemistry of these fulvenes was thus abandoned.



17 **18**

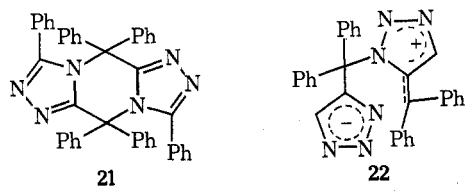
a, R = H
b, R = Ph
c, R = *p*-ClPh

17b, **17c**, and **18b** were stable in this solvent combination for >8 hr at −78° and exhibited λ_{max} at 463, 454, and 442 nm, respectively. Fulvenes **17b** and **18b** at −78° reacted slowly with methanol to give the subsequently characterized (methoxydiphenylmethyl)phenylazoles while **17b** rapidly provided the corresponding tertiary amine with piperidine at this temperature. If allowed to warm to 30° in solution, these fulvenes dimerized to give the photochemically inert 4*H*,10*H*-ditriazolo[1,2-*a*:1′,2′-*d*]pyrazines **19** and **20** or **21**, a decision between the latter two structures not being possible with the available spectral information.[13] A strong dependence of the rate of dimerization



19a, R = Ph
b, R = *p*-ClPh

20



21 **22**

Table I
Approximate Fulvene Lifetimes in Various Solvents (0.01 *M*) at −78° As Determined by Uv Absorption (Except for 17a)

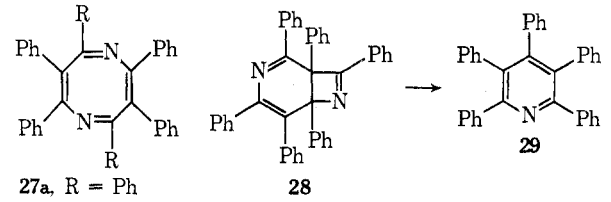
Fulvene	$\sim t_{1/2}$, min	Solvent
17a	<1	THF
17b	20	THF–MeCN (2:1)
	250	THF
	>500	THF–PhH (1:1)
18a	15	THF
18b	>500	THF–PhH (1:1)

Table II
Photoproduct Distribution

	Conversion, %					
Fulvene	**23** and **24**	**25**	**26**	**27**	**30**	Total
17b	50	7	11	26		94
18b	48	11	17	12	8	96
17c	67	14	7	5		93

on the solvent polarity was exhibited by both **17** and **18** and the 1,2,4-azafulvene system appeared to have a greater lifetime than its 1,2,3 congener in this respect (Table I). Since thermal [6 + 6] concerted cycloadditions occur in an unfavorable antarafacial manner, it may be assumed that this solvent effect is a result of stabilization of a transition state leading to a dipolar intermediate such as **22** in a nonconcerted dimerization. With regard to the observed stability differential between **17** and **18** with similar substitution, HMO theory reveals a greater π-charge density at position 1,4 relative to 2,3 in the highest occupied molecular orbital of the reference nonalternant hydrocarbon, fulvene, and one would therefore expect heteroatom replacement at 1,4 to be more effective than at 2,3 in increasing resonance energy.

Photolysis of 1,2,3- and 1,2,4-Triazafulvenes. Irradiation (Pyrex) of 0.025 *M* THF–benzene (1:1) solutions of either **17b** or **18b** at −78° resulted in the slow (4–5 hr) evolution of nitrogen and formation of a chromatographically separable mixture of benzonitrile (**23a**),[14] diphenylacetylene (**24**)[14] triphenylacrylonitrile (**25a**),[14,15] and 2,3-diphenylquinoline (**26a**)[14,16] in addition to a yellow, crystalline dimer (**27a**) of constitution $(C_{21}H_{15}N)_2$, mp 230–232° (see Table II). A hexaphenyl-1,5-diazocine structure **27a** has been assigned to this dimer based in part on the observation that thermolysis at 300° results in the formation of benzonitrile (63%) and pentaphenylpyridine[14,17] (**29**, 31%), a process which may proceed *via* the valence tautomer **28**. The mass spectrum (70 eV) displays major



27a, R = Ph
b, R = *p*-ClPh

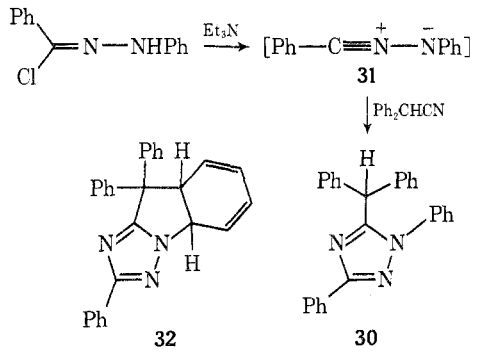
28 **29**

ions of *m/e* (rel intensity) 562 (100); M^+, 485 (10); M^+ − Ph, 459 (26); M^+ − PhCN, 383 (27); M^+ − PhCN − Ph, 281 (10); $M^+/2$ with a prominent doubly charged ion at 281.5 corresponding to MH^{2+}. This fragmentation parallels that reported for azocine[18] and 1,2-diazocine,[19] where mass spectral loss of HCN is a highly probable event (93 and 100%, respectively). The λ_{max} in EtOH occurred at 258 nm (ϵ 42,150) and showed a bathochromic shift to 263 nm (ϵ 37,000) in dilute ethanolic HCl and the reversible formation of a stable cation in 98% H_2SO_4 with λ_{max} 618

nm, the latter having possibly a diazabicyclo[5.1.0]octadienyl structure.[20]

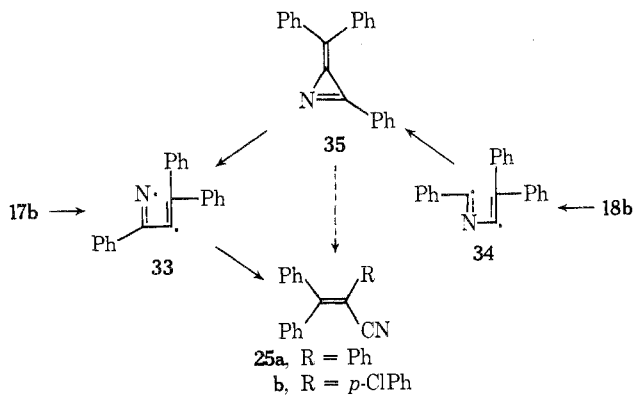
The photolysis of the *p*-chlorophenylfulvene **17c** under identical conditions afforded a mixture of *p*-chlorobenzonitrile (**23ab**), diphenylacetylene (**24**), 1-(*p*-chlorophenyl)-2,2-diphenylacrylonitrile[14,21] (**25b**), 2-(*p*-chlorophenyl)-3-phenylquinoline[14,22] (**26b**), and an analogous diazocine (**27b**), mp 243–244°. The latter compound had a mass spectrum (70 eV) of major ions at *m/e* (rel intensity) 634 (21); M^+ ($^{37}Cl_2$), 633 (38), 632 (82); M^+ ($^{37}Cl,^{35}Cl$), 631 (60), 630 (100); M^+ ($^{35}Cl_2$), 527 (12); M^+ − PhCN, 493 (16); M^+ − ClPhCN, 452 (13); M^+ − PhC_2Ph, 417 (46), M^+ − $ClPhC_2Ph$ in which the small but competitive loss of a nitrile *vs.* acetylene fragment is in contrast with that observed for **27a**. A hypsochromic effect of the chloro substituents on the various ultraviolet absorption maxima when compared to **27a** is apparent from the observation λ_{max} (EtOH) 247 nm (ϵ 36,750), λ_{max} (HCl-EtOH) 263 nm (ϵ 19,160), and λ_{max} (H_2SO_4) 525 nm.

Finally, 1,3-diphenyl-5-diphenylmethyl-1,2,4-triazole (**30**) was isolated from the photolysis of **18b** and identified by comparison with the product resulting from the addition of nitrile ylide[23] **31** to diphenylacetonitrile. A possible excited-state [$_\pi6_s$ + $_\pi6_s$] combination of **18b** with benzene to give **32** followed by an appropriate 1,3 shift and tautomerization may offer a suitable mechanistic rationalization for this product.

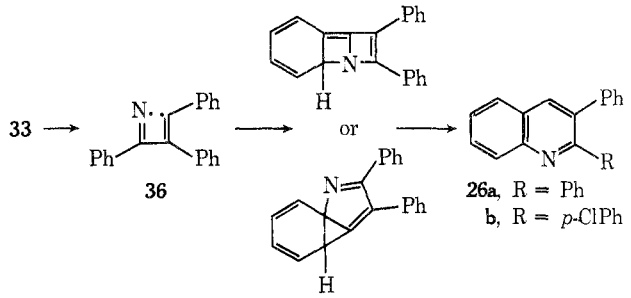


32 30

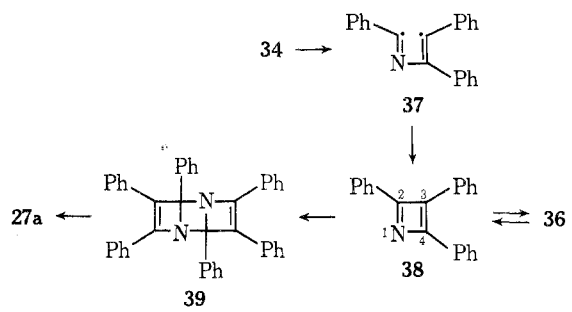
Mechanistic Considerations. The genesis of benzonitrile (or the *p*-chloro analog) and diphenylacetylene from initial fragmentation of the diradicals **33** and **34**, derived by photochemical loss of nitrogen from the respective fulvenes, and the rearrangement of **33** by a 1,2-phenyl shift[24] to a triphenylacrylonitrile are easily visualized. However,



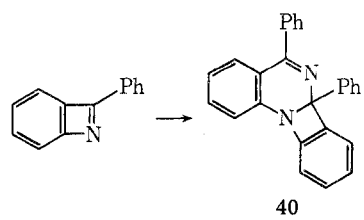
the conversion of **34** to **25** represents a substantial degree of bond reorganization and the most *direct* mechanistic pathway possible would seem to require the azatrifulvene **35** as an intermediate. The C–N bond cleavage necessary for the transformation of **35** to **25** *via* **33** has precedence derived from observations[24] on azirine thermal decomposition products.[25] The appearance of **26** as a common photoproduct seems to be the result of a 1,2-phenyl shift in **33** to give **36** followed by an appropriate cyclization and aromatization. However, the transformation of **34** to **36** may



not involve **35** but rather proceed *via* **37** to an intermediate triphenylazete (**38**) which then rearranges to **26a**, an argument which demands that the azete once formed always undergoes 1,2-bond cleavage (as opposed to the 3,4 alternative) in such a rearrangement. Such a proposal has the additional attractive feature that the origin of the diazocine **27a** may be viewed as a result of thermal electrocyclic ring opening[26] of a [$_\pi2_s$ + $_\pi4_s$] dimerization product **39** derived from **38**. Although the dimerization of **38** to give



ultimately a symmetrical diazocine could result from a 2,3-face combination, the proposed formation of a dimer with angular heteroatom sites is consistent with that recently observed for the dimerization of the benzoazete to 40.[27] It is interesting to note that only one dimer results



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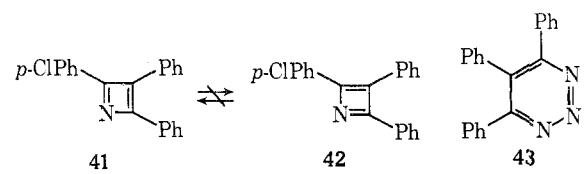
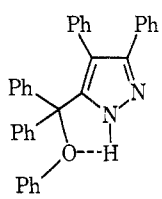
from the photolysis of **17c**, which may imply that the isomerization **41** ⇌ **42** is not occurring.



41 42 43

Support for the hypothesis that an intermediate such as **38** can lead to both **26** and **27** was received from our reexamination[28] of the photochemistry of triphenyl-*v*-triazine (**43**). Irradiation (Pyrex) of this latter triazine in benzene–THF (1:1) solution (0.025 *M*) at 30° for 5 hr gave, in addition to the previously reported benzonitrile and diphenylacetylene, both **27a** and **26a** (see Table II).

Synthesis of 1,2- and 2,3-Diazafulvenes. The addition of phenyllithium to methyl 3,4-diphenylpyrazole-5-carboxylate,[29] methyl 3,5-diphenylpyrazole-4-carboxylate,[30] and methyl 3,4-diphenylenepyrazole-5-carboxylate[31] followed by hydrolysis provided the requisite carbinols **44**, **45**, and **46**, whose conversions to the corresponding chlorodiphen-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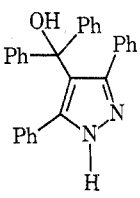
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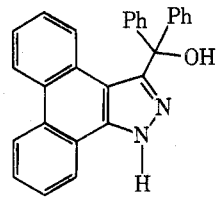
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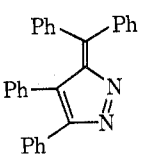
ylpyrazole hydrochlorides with thionyl chloride in benzene at 30° was unexceptional. Dehydrohalogenation of these salts with triethylamine in THF at −78° gave solutions of the corresponding fulvenes **47**, **48**, and **49** from which **47** and **49** could be isolated as stable, red, crystalline solids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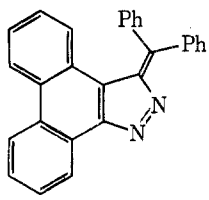
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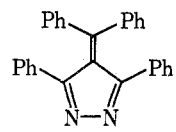
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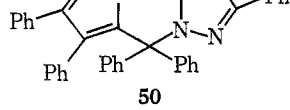
at room temperature. Diazafulvenes **47** and **49** displayed a λ_{max} (THF) at 393 and 382 nm, respectively, and both had similar mass spectral ions at m/e 385 ($M^+ + 1$), 384 (M^+), and 307 ($M^+ - C_6H_5$). While **49** appeared to be stable at its melting temperature of 155–156°, **47** in the solid state at 120–130° underwent dimerization to give **50**, mp 179–181°. Similarily, a 0.003 *M* solution of **47** in THF–benzene (1:1) upon photolysis (quartz) at 5° for 20 min gave **50** in high yield, while **49** was inert under these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conditions. Irradiation (Pyrex) of a THF–benzene (1:1) solution of **48** at −78° led to disappearance of the fulvene in 20 min with no gas evolution, but attempts to isolate the dimer in this case failed and only **46** was obtained.

Experimental Section[32]

5(4),α,α-Triphenyl-1,2,3-triazole-4(5)-methanol (8a). A solution of phenyllithium (0.573 mol) was prepared by the addition of 90 g (0.573 mol) of bromobenzene in 100 ml of anhydrous ether to 7.9 g (1.40 mol) of lithium ribbon (containing 1% sodium metal) in 400 ml of anhydrous ether. The solution, under a positive nitrogen atmosphere, was chilled to −78° and 37.5 g (0.185 mol) of methyl 4-phenyl-1,2,3-triazole-5-carboxylate[6] was added portionwise as a solid. The mixture was allowed to warm to room temperature, then refluxed for 18 hr, cooled, and decomposed using 150 ml of 5% aqueous hydrochloric acid. A fluffy white precipitate formed, which was collected by filtration and dried *in vacuo* to yield 21 g (35%) of **8a**, mp 218–221° dec. A sample recrystallized from benzene–ethanol melted at 220–221° dec: ir (KBr) 3300 cm^{-1} (broad OH and NH); nmr (DMSO-d_6) δ 7.83–6.92 (m, 15 H); mass spectrum (70 eV) m/e (rel intensity) 327 (100), 281 (67).

Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.84. Found: C, 77.19; H, 5.33; N, 12.84.

4(5),α,α-Triphenyl-1,2,3-triazole-5(4)-methanol (9a). The organic layer of the above filtrate was separated, washed with water, and dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. Upon diluting with pentane a fluffy white solid separated which was collected by filtration and dried to give 32 g (53%) of **9a**, mp 158–169° dec. Recrystallization from benzene twice afforded an analytical sample of **9a**: mp 159–160° dec; ir (KBr) 3320 (OH) and 3190 cm^{-1} (NH); nmr (DMSO-d_6) δ 7.70–6.82 (m, 15 H); mass spectrum (70 eV) m/e (rel intensity) 327 (100), 281 (23), and 250 (100).

Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.84. Found: C, 77.16; H, 5.36; N, 12.85.

Methyl 4-*p*-Chlorophenyl-1,2,3-triazole-5-carboxylate (7c). To a suspension of 13 g (0.2 mol) of sodium azide in 175 ml of dimethylformamide at room temperature was added dropwise a solution of 39 g (0.2 mol) of methyl *p*-chlorphenylpropiolate[33] in 50 ml of dimethylformamide. The addition was slightly exothermic (38°) and after it was complete (1 hr) the mixture was stirred for 18 hr at 30°. The solvent was removed *in vacuo*, and the residue was dissolved in 550 ml of water and washed with ether. The water layer was acidified with concentrated hydrochloric acid, extracted with ether, dried ($MgSO_4$), and filtered and the solvent was evaporated *in vacuo* to give 44 g (92%) of **7c**, mp 167–168°. Two recrystallizations from ethanol afforded an analytical sample: mp 170–171°; ir ($CHCl_3$) 3120 (NH), 1730 (C=O), 1140, 1098, 1015, and 838 cm^{-1}; nmr (DMSO-d_6) δ 8.08–7.42 (m, 4 H), 3.88 (s, 3 H); mass spectrum (70 eV) m/e (rel intensity) 239 (35), 237 (100), 208 (28), and 206 (79).

Anal. Calcd for $C_{10}H_8ClN_3O_2$: C, 50.54; H, 3.39; N, 17.58. Found: C, 50.71; H, 3.47; N, 17.57.

4(5)-*p*-Chlorophenyl-α,α-diphenyl-1,2,3-triazole-5(4)-methanol (8c). To a solution of phenyllithium (0.31 mol, prepared as above) in 300 ml of ether was added 23.8 g (0.1 mol) of the solid ester **7c** portionwise. After the initial exothermic reaction ceased, the mixture was refluxed for 18 hr and decomposed using 125 ml of 5% aqueous hydrochloric acid. After the layers were separated, the organic layer was washed with water, dried ($MgSO_4$), and filtered and the solvent was evaporated *in vacuo* to give 33.6 g (96%) of **8c**, mp 172–175°. An analytical sample was obtained upon recrystallization once from ethanol and once from benzene: mp 174–175°; ir ($CHCl_3$) 3420 (OH), 3170 (NH), 1492 (C=C), 1448 (C=C), 1095, 1010, 840, and 704 cm^{-1}; nmr (DMSO-d_6) δ 7.79–6.93 (m, 14 H); mass spectrum (70 eV) m/e (rel intensity) 363 (29), 361 (64), 317 (10), 315 (18), 286 (28), and 284 (100).

Anal. Calcd for $C_{21}H_{16}ClN_3O$: C, 69.71; H, 4.46; N, 11.61. Found: C, 69.59; H, 4.54; N, 11.63.

α,α-Diphenyl-1,2,3-triazole-4(5)-methanol (8b). A solution of phenyllithium (0.35 mol, prepared as above) in 400 ml of anhydrous ether was cooled to 5° and 13 g (0.093 mol) of solid ethyl 1,2,3-triazole-4(5)-carboxylate[7] was added portionwise. The mixture was refluxed for 18 hr and decomposed using 125 ml of saturated aqueous ammonium chloride solution. The ether layer was washed with water, dried ($MgSO_4$), and filtered and the solvent was evaporated *in vacuo* to give 20.5 g (88%) of **8b**, mp 184–186°. One recrystallization from benzene afforded an analytical sample: mp 185–186°; ir (KBr) 3277 (OH), 3178 (NH), 1658 (C=N), 1450 (C=C), 1123, 856, and 701 cm^{-1}; nmr (DMSO-d_6) δ 7.61 (s, 1 H) and 7.52–7.04 (m, 10 H); mass spectrum (70 eV) m/e (rel intensity) 251 (50), 174 (100), 105 (57), and 96 (68).

Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.21; N, 16.72. Found: C, 71.59; H, 5.27; N, 16.53.

5(4)-(9-Hydroxy-9-fluorene)-4(5)-phenyl-1,2,3-triazole (10). To a stirred solution of 0.034 mol of *o,o'*-dilithiobiphenyl[9] in 100 ml of anhydrous ether was added 0.034 mol of the lithium anion of methyl 4-phenyl-1,2,3-triazole-5-carboxylate[6] as an ether suspension. This was prepared by the addition of 20.4 ml (0.034 mol) of phenyllithium (1.66 *M*) to a solution of 6.9 g (0.034 mol) of the ester in 50 ml of anhydrous ether. After this suspension had been added, the mixture was refluxed for 18 hr and then decomposed using 5% aqueous hydrochloric acid (125 ml). The organic layer was washed with water (2 × 50 ml), dried ($MgSO_4$), and filtered and the solvent was evaporated *in vacuo*, yielding 6.2 g (56%) of **10**, mp 216–219°. Two recrystallizations from ether–pentane afforded an analytical sample: mp 219–220°; ir (KBr) 3210 cm^{-1} (NH and OH, broad); nmr (DMSO-d_6) δ 7.87–6.48 (m, 13 H); mass spectrum (70 eV) m/e (rel intensity) 325 (40), 181 (54), and 152 (100).

Anal. Calcd for $C_{21}H_{15}N_3O$: C, 77.52; H, 4.65; N, 12.92. Found: C, 77.35; H, 4.75; N, 12.83.

α,α-Diphenyl-1,2,4-triazole-3(5)-methanol (11). A solution of phenyllithium (1.0 mol, prepared as above) in 1 l. of ether was chilled in an ice bath to 5° and 38.1 g (0.3 mol) of solid methyl 1,2,4-triazole-3-carboxylate (**10**) was added portionwise under a positive nitrogen atmosphere. The mixture was allowed to come to 30° and then refluxed for 18 hr. The reaction mixture was then decomposed by the addition of 250 ml of saturated aqueous ammonium chloride solution to yield a heavy precipitate, which was removed by filtration and dried *in vacuo* to give 32 g (42%) of **11**, mp 215–218°. From the filtrate, the organic layer was washed with water, dried ($MgSO_4$), and filtered and the solvent was evaporated *in vacuo* to give 11 g of triphenylcarbinol, mp 154–156°.[14] The water layers were combined and neutralized with aqueous hydrochloric acid to pH 7, after which the crystals formed were

removed by filtration to give an additional 18 g (24%) of **11**, mp 218–220°. These two crops were combined and recrystallized from benzene to give a total of 47 g (62%) of **11**, mp 221–223°. An analytical sample was obtained by recrystallization from benzene: mp 222–223°; ir (KBr) 3380 (NH) and 3150 cm^{-1} (OH); nmr (DMSO-d_6) δ 8.28 (s, 1 H) and 7.82–7.03 (m, 10 H); mass spectrum (70 eV) *m/e* (rel intensity) 251 (100), 233 (44), 174 (80), 105 (51), and 96 (38).

Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.21; N, 16.72. Found: C, 71.79; H, 5.26; N, 16.63.

1-Benzyl-3-phenyl-1,2,4-triazole (14). To a magnetically stirred solution of 26.5 g (0.39 mol) of sodium ethoxide in 100 ml of ethanol was added portionwise 50.8 g (0.35 mol) of 3-phenyl-1,2,4-triazole.[11] The mixture was stirred for 5 min and 66.7 g (0.525 mol) of freshly distilled benzyl chloride was added. The reaction mixture was refluxed for 1 hr and then stirred at 30° for an additional 18 hr. The sodium chloride formed was removed by filtration and the filtrate was concentrated *in vacuo*, yielding an oily suspension of crystals. The oil was decanted and the solid was crystallized from toluene–pentane to give 41 g (50%) of **14**, mp 100–102°. A second crop crystallized from the oil and was removed by filtration, affording an additional 13 g (16%) of **14**, mp 98–100°. Recrystallization from toluene–pentane gave an analytical sample: mp 101–102°; ir ($CHCl_3$) 2987 (CH), 1496 (C=C), 1440 (C=C), and 695 cm^{-1}; nmr ($CDCl_3$) δ 8.32–8.03 (m, 2 H), 7.94 (s, 1 H), 7.53–7.00 (m, 8 H), and 5.17 (s, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 235 (100) and 91 (66).

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.54; H, 5.60; N, 17.92.

1-Benzyl-3,α,α-triphenyl-1,2,4-triazole-5-methanol. A solution of phenyllithium (0.25 mol, prepared as above) in 200 ml of anhydrous ether was cooled to −20° and treated over 1 hr with a solution of 52 g (0.22 mol) of **14** in 200 ml of tetrahydrofuran–anhydrous ether (1:1 v/v). The mixture was stirred for 2 hr without external cooling and a solution of 41.9 g (0.23 mol) of benzophenone in 100 ml of tetrahydrofuran was added dropwise over 1 hr. After stirring for 18 hr at 30°, water (300 ml) was added dropwise and the resulting layers were separated. The organic layer was washed with water (2 × 50 ml), dried ($MgSO_4$), and filtered and the solvent was evaporated *in vacuo* to give 49 g (53%) of the alcohol, mp 118–121°.

An analytical sample was obtained upon recrystallization from benzene: mp 120–122°; ir ($CHCl_3$) 3380 (OH), 3060, 3000, 1595, 1487, 1483, and 687 cm^{-1}; nmr (DMSO-d_6) δ 8.14–7.78 (m, 2 H), 7.67–6.88 (m, 18 H), and 5.47 (s, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 417 (21), 326 (10), 235 (100), 182 (84), 105 (79), 91 (90).

Anal. Calcd for $C_{28}H_{23}N_3O$: C, 80.55; H, 5.55; N, 10.07. Found: C, 80.62; H, 5.64; N, 10.08.

3(5),α,α-Triphenyl-1,2,4-triazole-5(3)-methanol (15). A stirred solution of 47 g (0.11 mol) of the above alcohol in 300 ml of liquid ammonia (−50°) was treated portionwise over 1.5 hr with 6.2 g (0.26 mol) of sodium metal. After the addition was complete, the reaction mixture was stirred for 2.5 hr and quenched by the addition of 15.5 g (0.29 mol) of solid ammonium chloride. The ammonia was allowed to evaporate and the residue was partitioned between ether and water. The ether layer was washed with water (2 × 100 ml), dried ($MgSO_4$), filtered, and concentrated to 50 ml on a steam bath. Upon diluting with pentane, a precipitate formed which was removed by filtration and dried *in vacuo* to give 21 g (58%) of **15**, mp 228–230° dec. The mother liquors were then evaporated to dryness to give an additional 16 g (34%). The carbinol **15** was recrystallized twice from toluene to afford an analytical sample: mp 232–233° dec; ir (KBr) 3043 (NH), 3263 (OH), 1490, 1468, 746, and 691 cm^{-1}; nmr (DMSO-d_6) δ 8.12–7.82 (m, 2 H) and 7.58–6.82 (m, 13 H); mass spectrum (70 eV) *m/e* (rel intensity) 327 (20), 310 (67), 209 (100), 281 (12), 250 (21), 182 (23), 178 (51), 105 (43) and 103 (44).

Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.84. Found: C, 77.22; H, 5.38; N, 12.89.

4(5)-Phenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole Hydrochloride. To a solution of 40 ml of thionyl chloride in 60 ml of benzene was added 21 g (0.095 mol) of the alcohol **8c**. The mixture was stirred for 3 hr at 30°, heated to reflux for 1 hr, and then stirred at 30° for 18 hr. Upon diluting with anhydrous ether a solid separated which was collected by filtration to give 24 g (66%) of the salt, mp 228–230° dec. An additional 9 g (24%), mp 222–226° dec, was recovered by evaporating the filtrate and diluting the residue with ether. A sample recrystallized from tetrahydrofuran–ether had mp 229–230° dec; ir (KBr) 3270, 2340, and 1852 (NH), 759 cm^{-1} (CCl); mass spectrum (70 eV) *m/e* (rel intensity 345 (7), 281 (100), 282 (100), 283 (89), and 204 (46).

Anal Calcd for $C_{21}H_{16}ClN_3 \cdot HCl$: C, 65.97; H, 4.48; N, 10.99. Found: C, 65.90; H, 4.40; N, 11.12.

5(4)-Chlorodiphenylmethyl-1,2,3-triazole Hydrochloride. To a stirred solution of 40 ml of thionyl chloride in 60 ml of benzene was added portionwise 24.5 g (0.097 mol) of the solid alcohol **8b**. The mixture was stirred for 1 hr at 30°, during which time complete solution occurred, followed by formation of a heavy precipitate. The reaction mixture was diluted with ether and the solid was removed by filtration and dried *in vacuo* to give 25.8 g (84%) of the salt, mp 136–140°. An analytically pure sample could not be prepared, as this salt was very hydroscopic: ir (KBr) 3310, 2560, and 1845 (NH^+), 1579 (C=N), 1483 (C=C), 1443 (C=C), 750 (CCl), and 698 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 233 (100), 205 (44), and 128 (24).

4(5)-*p*-Chlorophenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole Hydrochloride. To a solution of 15 ml of thionyl chloride in 30 ml of benzene was added 9.05 g (0.025 mol) of the alcohol **8c**. The mixture was stirred at 30° for 18 hr and then refluxed for 4 hr. Upon dilution with ether a precipitate formed which was removed by filtration and dried *in vacuo* to give 9.1 g (87%) of the salt, mp 245–248° dec. Two recrystallizations from tetrahydrofuran–ether afforded the analytical sample: mp 250–252°; ir (KBr) 3310, 2520, and 1830 ($NH \cdot HCl$), 1602 (C=N), 1490 and 1443 (C=C), 750 (CCl), and 698 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 345 (30), 343 (100), 268 (50), and 266 (20).

Anal. Calcd for $C_{21}H_{15}Cl_2N_3 \cdot HCl$: C, 60.52; H, 3.87; N, 10.08. Found: C, 60.47; H, 3.92; N, 10.19.

3(5)-Chlorodiphenylmethyl-1,2,4-triazole Hydrochloride. To a solution of 60 ml of thionyl chloride in 100 ml of benzene was added 38 g (0.15 mol) of the solid alcohol **11** portionwise. After the exothermic reaction ceased, the mixture was stirred for 18 hr at 30°. The solid which formed was removed by filtration and dried *in vacuo* to give 33 g (73%) of the salt, mp 184–187°. Two recrystallizations from tetrahydrofuran–ether afforded a sample which had mp 186–188°. An analytically pure sample could not be prepared, as this salt was very hydroscopic: ir (KBr) 3300, 2460, and 1890 (NH^+) and 760 cm^{-1} (CCl); mass spectrum (70 eV) *m/e* (rel intensity) 233 (100), 205 (40), and 128 (35).

3(5)-Phenyl-5(3)-chlorodiphenylmethyl-1,2,4-triazole Hydrochloride. A stirred solution of 9.8 g (0.03 mol) of the alcohol **15** in 100 ml of anhydrous ether was saturated with dry hydrogen chloride. The solvent was evaporated *in vacuo* and the residue was treated with a solution of 15 ml of thionyl chloride in 30 ml of benzene. The resulting mixture was refluxed for 1 hr and then stirred at 30° for 18 hr. Upon dilution with anhydrous ether, the crystals which formed were collected by filtration and dried *in vacuo* to give 10.8 g (93%) of the salt, mp 174–176° dec. Two recrystallizations from tetrahydrofuran–ether afforded an analytical sample: mp 175–177°; ir (KBr) 3300, 2380, and 1840 (NH^+) and 780 cm^{-1} (CCl); mass spectrum (70 eV) *m/e* (rel intensity) 309 (100).

Anal. Calcd for $C_{21}H_{16}ClN_3 \cdot HCl$: C, 65.97; H, 4.48; N, 10.99. Found: C, 65.91; H, 4.54; N, 11.12.

1,6-Diphenyl-5,5,10,10-bisdiphenylene-5*H*,10*H*-ditriazolo[1,2-*a*;1′,2′-*d*]pyrazine (16). To a stirred solution of 10 ml of thionyl chloride in 50 ml of dry benzene was added 3.25 g (0.01 mol) of the alcohol **10**. The solution was heated to reflux in order to complete solution, and after 10 min a heavy precipitate formed. Heating was continued for 0.5 hr and the suspension was then stirred for 18 hr at 30°. The reaction was diluted with dry ether, and the solid was removed by filtration, washed with ether, and dried *in vacuo* to give 3 g (97%) of **16**: mp >330°; ir (KBr) 1450 (C=C), 1280, 943, 900, 745, and 700 cm^{-1}; nmr (DMSO-d_6) δ 7.81–6.98 (m, 26 H); mass spectrum (70 eV) *m/e* (rel intensity) 279 (100).

Anal. Calcd for $C_{42}H_{26}N_6$: C, 82.06; H, 4.26; N, 13.67. Found: C, 82.14; H, 4.22; N, 13.81.

Attempted Synthesis of 4(5)-Benzhydrylidene-4*H*(5*H*)-1,2,3-triazole (17a). To a chilled solution (−78°) of 1.16 g (0.0037 mol) of 5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride in 200 ml of benzene–tetrahydrofuran (1:1 v/v) was added 0.75 g (0.0074 mol) of triethylamine. A deep orange solution formed during the addition of the second equivalent of triethylamine but began to fade immediately at −78°. The resulting colorless solution (after 5 min) was filtered through Celite to remove the triethylamine hydrochloride (0.92 g, 91%), and from the filtrate only 0.85 g (91%) of **8b**, mp 184–186°,[14] could be isolated.

Attempted Synthesis of 3(5)-Benzhydrylidene-3*H*(5*H*)-1,2,4-triazole (18a). To a chilled suspension (−78°) of 3.06 g (0.01 mol) of 3(5)-chlorodiphenylmethyl-1,2,4-triazole hydrochloride in 300

ml of benzene–tetrahydrofuran (1:1 v/v) was added 2.02 g (0.02 mol) of triethylamine. The resulting intense yellow solution at −78° faded over 4 hr and the resulting colorless solution was filtered through Celite to remove the triethylamine hydrochloride (2.35 g, 85%). The solvent from the filtrate was evaporated *in vacuo*, yielding a gummy residue of which only 2.25 g (89%) of **11**, mp 218–220°,[14] could be isolated.

2,5,5,7,10,10-Hexaphenyl-5*H*,10*H*-ditriazolo[1,2-*a*:1′,2′-*d*]pyrazine (20). A chilled solution (−78°) of 1.91 g (0.005 mol) of 3(5)-phenyl-5(3)-chlorodiphenylmethyl-1,2,4-triazole hydrochloride in 200 ml of anhydrous tetrahydrofuran was treated with 1.01 g (0.01 mol) of triethylamine. An intense red-orange color formed during the addition of the second equivalent of triethylamine and the solution was allowed to warm to room temperature, during which time the color faded. The reaction mixture was diluted with 200 ml of anhydrous ether and filtered through Celite to remove 1.25 g (91%) of triethylamine hydrochloride. The solvent was evaporated *in vacuo* to give 1.26 g (84%) of pure **20:** mp 291–293°; ir 1501 and 1456 (C=C), 905, and 701 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 590 (17), 562 (30), 281 (100), and 204 (48).

Anal. Calcd for $C_{42}H_{30}N_6$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.23; H, 4.99; N, 13.45.

Attempted Photolysis of 20. A solution of 1.55 g (0.0025 mol) of the pyrazine **20** in 400 ml of benzene–tetrahydrofuran (1:1 v/v) was photolyzed for 4 hr using a Hanovia 450-W high-pressure mercury discharge lamp in a quartz probe. There was no nitrogen evolution and, upon evaporating the solvent *in vacuo*, starting material was recovered quantitatively.[14]

Hydrolysis of 20. To a suspension of 0.618 g (0.001 mol) of the pyrazine **20** in 200 ml of ethanol was added 50 ml of 5% hydrochloric acid. The mixture was refluxed for 18 hr and evaporated *in vacuo*. The residue was dissolved in ether, washed with water, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give 0.56 g (91%) of crystalline **15**, mp 232–233°.[14]

3(5)-Phenyl-5(3)-methoxydiphenylmethyl-1,2,4-triazole. A solution of 3.83 g (0.01 mol) of 3(5)-phenyl-5(3)-chlorodiphenylmethyl-1,2,4-triazole hydrochloride in 250 ml of anhydrous tetrahydrofuran was cooled to −78° and treated dropwise with 2.02 g (0.02 mol) of anhydrous triethylamine, during which time a deep red-orange color developed. After stirring for 10 min at −78°, the reaction mixture was diluted with hexane and filtered under a dry nitrogen atmosphere to remove 2.58 g (94%) of triethylamine hydrochloride. The resulting clear red-orange solution was treated with 40 ml of anhydrous methanol at −78° and allowed to warm gradually to room temperature. As the reaction mixture warmed, there was a gradual discharge of color until a clear, colorless solution resulted from which the solvent was evaporated *in vacuo*. The solid residue was recrystallized from toluene to give 2.9 g (89%) of the ether: mp 134–135°; ir ($CHCl_3$) 3444 (NH), 1490, 1468, and 1443 (C=C), 1100 (broad, COC), and 698 cm^{-1}; nmr ($CDCl_3$) δ 8.28–7.92 (m, 2 H), 7.77–7.06 (m, 13 H), and 3.22 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 341 (70) and 310 (100).

Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.39; H, 5.61; N, 12.31. Found: C, 77.42; H, 5.80; N, 12.15.

1,5,5,6,10,10-Hexaphenyl-5*H*,10*H*-ditriazolo[1,2-*a*:1′,2′-*d*]pyrazine (19a). A solution of 2 g (0.0052 mol) of 4(5)-phenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride in 200 ml of anhydrous tetrahydrofuran was chilled to −78° and treated with 1.05 g (0.01 mol) of triethylamine. An intense blood-red color formed during the addition of the second equivalent of triethylamine. The solution was allowed to warm to room temperature and the color faded gradually. The reaction was diluted with 200 ml of anhydrous ether and filtered through Celite to remove 1.22 g (89%) of triethylamine hydrochloride. The solvent was evaporated *in vacuo* to give 1.6 g (87%) of **19a:** mp 277–280°; λ_{max} (THF) 216 nm (ε 30,282); ir (KBr) 1494 and 1449 (C=C) and 895 and 698 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 590 (15), 562 (23), 281 (100), and 204 (50).

Anal. Calcd for $C_{42}H_{30}N_6$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.29; H, 4.93; N, 13.57.

Attempted Photolysis of 19a. A solution of 1.55 g (0.0025 mol) of pyrazine **19a** in 400 ml of benzene–tetrahydrofuran (1:1) was photolyzed for 3 hr using a Hanovia 450-W high-pressure mercury discharge lamp in a quartz probe. There was no nitrogen evolution and upon evaporating the solvent *in vacuo*, starting material was recovered quantitatively.[14]

Hydrolysis of 19a. To a suspension of 0.618 g (0.001 mol) of the pyrazine **19a** in 200 ml of ethanol was added 50 ml of 5% hydrochloric acid. The mixture was refluxed for 18 hr and the solvent was evaporated *in vacuo*. The residue was dissolved in ether, washed with water, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Upon diluting with pentane 0.52 g (87%) of **8a** precipitated.[14]

4(5)-Phenyl-5(4)-diphenylpiperidinomethyl-1,2,3-triazole. A solution of 1 g (0.0025 mol) of 4(5)-phenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride in 200 ml of anhydrous tetrahydrofuran was chilled to −78° and treated with 0.5 g (0.005 mol) of triethylamine. There was an immediate red color and precipitate formation and the solution was filtered through Celite under a dry nitrogen atmosphere to remove 0.65 g (94%) of triethylamine hydrochloride. When the resulting clear blood-red solution was treated with 8.5 g (0.1 mol) of piperidine there resulted an immediate discharge of color. The solvent was evaporated *in vacuo* and the solid residue was recrystallized from benzene–hexane to give 0.85 g (95%) of colorless needles of the amine: mp 148–149°; ir ($CHCl_3$) 3410 (NH), 2935 (CH), 1445, 1490, and 695 cm^{-1}; nmr ($CDCl_3$) δ 7.55–6.68 (m, 15 H), 3.01–2.49 (m, 4 H), and 1.69–1.38 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 281 (100), 85 (29), and 84 (41).

Anal. Calcd for $C_{23}H_{26}N_4$: C, 77.06; H, 7.31; N, 15.63. Found: C, 77.24; H, 7.28; N, 15.82.

4(5)-Phenyl-5(4)-methoxydiphenylmethyl-1,2,3-triazole. A solution of 3.83 g (0.01 mol) of 4(5)-phenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride in 250 ml of anhydrous tetrahydrofuran was cooled to −78° and treated dropwise with 2.02 g (0.02 mol) of anhydrous triethylamine, during which time a deep red color developed. After stirring for 10 min the reaction mixture was diluted with hexane and filtered under a dry nitrogen atmosphere to remove 2.70 g (100%) of triethylamine hydrochloride. The resulting clear deep-red solution was treated with 20 ml of anhydrous methanol at −78° and allowed to warm gradually to 30°. As the reaction mixture warmed, there was a gradual discharge of color until a clear colorless solution resulted from which the solvent was evaporated *in vacuo*. The solid residue was crystallized from benzene–hexane to afford 3.2 g (94%) of the ether: mp 101–102°; ir ($CHCl_3$) 3437 (NH) and 1075 cm^{-1} (COC); nmr ($CDCl_3$) δ 7.66–6.98 (m, 15 H) and 3.07 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 341 (60) and 310 (100).

Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.39; H, 5.61; N, 12.31. Found: C, 77.41; H, 5.68; N, 12.09.

Photolysis of 5(4)-Phenyl-4(5)-benzhydrylidene-4*H*(5*H*)-1,2,3-triazole (17b). A chilled solution (−78°) of 3.83 g (0.01 mol) of 4(5)-phenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride in 400 ml of benzene–tetrahydrofuran (1:1) was treated with 2.02 g (0.02 mol) of triethylamine. The resulting blood-red solution, λ_{max} (THF) 463 nm, of the fulvene **17b** was filtered through Celite to remove 1.35 g (98%) of triethylamine hydrochloride and then photolyzed at −78° for 5 hr using a 450-W Hanovia high-pressure mercury discharge lamp in a Pyrex probe. The solvent was evaporated *in vacuo* and the residue was triturated with benzene to give 0.73 g (26%) of **27a**, mp 225–230°. After recrystallization from ethanol an analytical sample was obtained: mp 230–232°; λ_{max} (EtOH) 258 nm (ε 42,150); λ_{max} (HCl-EtOH) 263 nm (ε 36,998); λ_{max} (concentrated H_2SO_4) 618 nm; ir ($CHCl_3$) 1618 (C=N), 1598 (C=C), 1577 (C=C), 1492, 1448, 1125 (broad), and 698 cm^{-1}; nmr ($CDCl_3$) δ 8.08–6.57 (m, 30 H); mass spectrum (70 eV) *m/e* (rel intensity) 563 (50), 562 (100), 483 (6), 459 (18), 383 (21), 281 (100), 204 (48), and 178 (14).

Anal. Calcd for $C_{42}H_{30}N_2$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.55; H, 5.39; N, 4.99.

The benzene triturate was concentrated *in vacuo* and the residue was chromatographed on 50 g of Florisil. Upon elution with hexane 0.87 g of diphenylacetylene was isolated.[14] Elution with hexane–benzene (1:1) afforded 0.53 g of benzonitrile.[14] Further elution with pure benzene gave 0.20 g (7%) of triphenylacrylonitrile **35**, mp 166–167°.[14,15] The last compound present, 0.31 g (11%), was isolated by elution with benzene–chloroform (8:2–7:3 v/v) and was identified as 2,3-diphenylquinoline **26a**, mp 90–91°.[14,16]

Photolysis of 3(5)-Phenyl-5(3)-benzhydrylidene-5*H*(3*H*)-1,2,4-triazole (18b). A chilled solution (−78°) of 3.83 g (0.01 mol) of 3(5)-phenyl-5(3)-chlorodiphenylmethyl-1,2,4-triazole hydrochloride in 400 ml of benzene–tetrahydrofuran (1:1) was treated with 2.02 g (0.02 mol) of triethylamine. The resulting red-orange solution, λ_{max} (THF) 442 nm, of the fulvene **18b** was filtered through Celite to remove 2.62 g (92%) of triethylamine hydrochloride and then photolyzed at −78° for 4.5 hr using a 450-W Hanovia high-pressure mercury discharge lamp in a Pyrex probe. The resulting colorless solution was allowed to warm to room temperature and was concentrated *in vacuo*. The residue was triturated

with benzene to give 0.338 g of **27a**, mp 225–230°. The benzene triturate was evaporated *in vacuo* and the residue was chromatographed on 50 g of Florisil. Upon elution with hexane 0.85 g of diphenylacetylene was isolated.[14] Elution with hexane–benzene (1:1) afforded 0.45 g of benzonitrile.[14] Further elution with benzene gave 0.30 g of triphenylacrylonitrile **35**, mp 166–167°.[14,15] Continued elution with benzene–chloroform (1:1) led to the isolation of 0.309 g of 1,3-diphenyl-5-diphenylmethyl-1,2,4-triazole (**30**), mp 188–190°.[14] The last compound present, 0.48 g, was isolated by eluting with benzene–chloroform (8:2–7:3 v/v) and was identified as 2,3-diphenylquinoline **26a**, mp 90–91°.[14,16]

Thermolysis of 27a. The dimer **27a** (0.56 g, 0.001 mol) was heated at 300° for 1 hr in a 100-ml flask. The residue was chromatographed on 15 g of Florisil and elution with hexane–benzene (1:1 v/v) gave 0.027 g (26%) of benzonitrile.[14] elution with benzene gave 0.059 g (13%) of pentaphenylpyridine, mp 244–245°.[14,17] Further elution with benzene afforded 0.326 g (58%) of the starting dimer **27a**.

Photolysis of 4(5)-*p*-Chlorophenyl-5(4)-benzhydrylidene-5*H*(4*H*)-1,2,4-triazole (17c). A chilled (−78°) solution of 4.17 g (0.01 mol) of 4(5)-*p*-chlorophenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride in 400 ml of benzene–tetrahydrofuran (1:1) was treated with 2.02 g (0.02 mol) of triethylamine. The resulting red-orange solution, λ_{max} (THF) 454 nm, of the fulvene **17c** was filtered to remove the triethylamine hydrochloride (2.43 g, 88%) and then photolyzed at −78° for 3.5 hr using a 450-W Hanovia high-pressure mercury discharge lamp in a Pyrex probe. The resulting colorless solution was concentrated *in vacuo* and the residue was triturated with benzene and allowed to stand for 24 hr, during which time 0.160 g of **27b** crystallized, mp 243–244°. After two recrystallizations from ethanol **27b** had λ_{max} (EtOH) 247 nm (ε 36,750); λ_{max} (HCl–EtOH) 263 nm (ε 19,163); λ_{max} (H_2SO_4) 525 nm; ir ($CHCl_3$) 1620 (C=N), 1592 and 1485 (C=C), 1445, 1140, 1125 (broad), 1090, and 695 cm^{-1}; nmr ($CDCl_3$) δ 8.05–6.84 (m, 30 H); mass spectrum (70 eV) *m/e* (rel intensity) 634 (21), 633 (38), 632 (82), 631 (60), 630 (100), 495 (7), 494 (10), 493 (16), 492 (14), 454 (6), 452 (13), 419 (21), 417 (46), 214 (15), 212 (40), and 178 (45).

Anal. Calcd for $C_{42}H_{28}Cl_2N_2$: C, 79.87; H, 4.47; N, 4.44. Found: C, 79.94; H, 4.52; N, 4.46.

The benzene triturate was evaporated *in vacuo* and the residue was chromatographed on 50 g of Florisil. Upon elution with hexane 1.17 g of diphenylacetylene was isolated.[14] Elution with hexane–benzene (1:1 v/v) afforded 0.938 g of *p*-chlorobenzonitrile.[14] Further elution with benzene gave 0.447 g of 1-*p*-chlorophenyl-2,2-diphenylacrylonitrile (**25b**), mp 142–143°.[14,21] Continued elution with benzene–chloroform (9:1–7:3) led to the isolation of 0.221 g of 2-*p*-chlorophenyl-3-phenylquinoline (**26b**), mp 93–95°.[14]

2-*p*-Chlorophenyl-3-phenylquinoline-4-carboxylic Acid. To a solution of 7.35 g (0.05 mol) of isatin and 12.7 g (0.055 mol) of 4-chloro-α-phenylacetophenone[34] in 60 ml of dry ethanol was added 12 g of sodium hydroxide in 25 ml of water. The mixture was refluxed for 18 hr and cooled and the solvent was evaporated *in vacuo*. The residue was dissolved in water, washed with ether, decolorized with Norite, filtered, and acidified with concentrated hydrochloric acid. The precipitate which formed was removed by filtration and dried *in vacuo* to give 16.5 g (92%) of the carboxylic acid, mp 305–308°. An analytical sample obtained by two recrystallizations from ethanol had mp 307–308°; ir (KBr) 3400 (OH) and 1715 cm^{-1} (C=O); nmr (DMSO-d_6) δ 8.33–7.08 (m, 13 H); mass spectrum (70 eV) *m/e* (rel intensity) 361 (27), 360 (48), 359 (73), 358 (92), 316 (14), 315 (23), 314 (38), 313 (35), 280 (22), 279 (84), 278 (100), and 277 (52).

Anal. Calcd for $C_{22}H_{14}ClNO_2$: C, 73.44; H, 3.92; N, 3.89. Found: C, 73.46; H, 4.04; N, 3.96.

2-*p*-Chlorophenyl-3-phenylquinoline (26b). In a 100-ml flask, 3.6 g (0.01 mol) of the above acid was heated at 320° until gas evolution ceased. The residue was chromatographed over 20 g of Florisil and elution with benzene gave 2.46 g (78%) of **26b**, mp 93–95°. One recrystallization from pentane afforded an analytical sample: mp 94–95°; ir ($CHCl_3$) 3060, 2975, 1597, 1488, 1095, 1018, 841, 701, and 597 cm^{-1}; nmr ($CDCl_3$) δ 8.33–7.10 (m, 14 H); mass spectrum (70 eV) *m/e* (rel intensity) 317 (21), 316 (47), 315 (61), and 314 (100).

Anal. Calcd for $C_{21}H_{14}ClN$: C, 79.87; H, 4.47; N, 4.44. Found: C, 79.76; H, 4.55; N, 4.44.

1,3-Diphenyl-5-diphenylmethyl-1,2,4-triazole (30). A 250-ml, three-necked, round-bottomed flask fitted with a reflux condenser, nitrogen inlet, and pressure-equalizing dropping funnel was charged with 9.24 g (0.04 mol) of benzoyl chloride phenylhydrazone[23] and 15.44 g (0.08 mol) of diphenylacetonitrile and then heated to 100°. The resulting solution was treated dropwise over 3 hr at 100° with a solution of 14.54 g (0.144 mol) of triethylamine in 30 ml of toluene. After the addition was complete, the reaction mixture was stirred at reflux for 18 hr, cooled, and diluted with benzene to 250 ml and the precipitated triethylamine hydrochloride was removed by filtration. The organic layer was washed with water (300 ml), dried ($MgSO_4$), decolorized with Norite, filtered, and evaporated *in vacuo*. The residue was dissolved in hot ethanol and diluted with water until turbid. After standing for 18 hr, needles formed and were removed by filtration and recrystallized from ethanol to give 10.4 g (67%) of **30**: mp 188–190°; ir ($CHCl_3$) 1600 (C=N), 1498 (C=C), 1448 (C=C), 1353, and 697 cm^{-1}; nmr ($CDCl_3$) δ 8.35–8.11 (m, 2 H), 7.87–6.98 (m, 18 H), and 5.49 (s, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 387 (100).

Anal. Calcd for $C_{27}H_{21}N_3$: C, 83,69; H, 5.46; N, 10.85. Found: C, 83.72; H, 5.39; N, 10.72.

Photolysis of Triphenyl-*v*-triazine (43). A solution of 3.09 g (0.01 mol) of triphenyl-*v*-triazine[28] in 400 ml of benzene–tetrahydrofuran (1:1 v/v) was photolyzed at 30° for 6 hr using a Hanovia 450-W high-pressure mercury discharge lamp in a Pyrex probe. After removing the solvent *in vacuo*, the residue was triturated with benzene–pentane to afford yellow crystals which were removed by filtration and dried *in vacuo* to give 0.51 g (18%) of **27a**, mp 232–234°.[14] The triturate was evaporated *in vacuo* and the residue was chromatographed over 40 g of Florisil. Upon elution with hexane 1.21 g of diphenylacetylene was isolated.[14] Elution with hexane–benzene (1:1 v/v) provided 0.68 g of benzonitrile.[14] Continued elution with benzene–chloroform (9:10–7:3) gave 0.170 g of 2,3-diphenylquinoline.[14,16]

3,5,α,α-Tetraphenylpyrazole-4-methanol (45). To a solution of phenyllithium (0.2 mol, prepared as above) and sodium in 250 ml of anhydrous ether was added portionwise 13 g (0.0468 mol) of solid methyl 3,5-diphenylpyrazole-4-carboxylate.[30] The suspension was stirred for 18 hr at reflux and decomposed with 100 ml of 5% aqueous hydrochloric acid. A solid separated and was removed by filtration to give 16.8 g of **45**, mp 207–209°. The organic layer of the filtrate was washed with water (2 × 75 ml), dried ($MgSO_4$), decolorized with Norite (2 g), filtered through Celite, and evaporated *in vacuo* to give an additional 1.4 g of **45**, mp 208–209°. The combined yield was 18.4 g (97%) and an analytical sample of **45** obtained by crystallization from toluene had mp 208–209°; ir (KBr) 3490 (broad OH) and 3230 cm^{-1} (broad NH); nmr (DMSO-d_6) δ 12.97 (broad s, 1 H), 7.52–6.61 (m, 20 H), and 6.19 (s, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 402 (40), 385 (100), and 325 (40).

Anal. Calcd for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96. Found: C, 83.29; H, 5.61; N, 7.04.

3,5-Diphenyl-4-chlorodiphenylmethylpyrazole Hydrochloride. A solution of 8.04 g (0.02 mol) of the alcohol **45** in 100 ml of tetrahydrofuran was saturated with dry hydrogen chloride. The mixture was stirred for 15 min, the solvent was evaporated *in vacuo*, and the residue was treated with a solution of 15 ml of thionyl chloride in 30 ml of dry benzene. After heating at reflux for 0.5 hr the mixture was stirred at 30° for 18 hr. The precipitate that formed was removed by filtration, washed with ether, and dried *in vacuo* to give 6 g (66%) of the salt, mp 168–171°. A second crop crystallized, affording an additional 2 g (22%), mp 168–170°. An analytical sample obtained by crystallization from tetrahydrofuran ether had mp 170–171°; ir (KBr) 3060, 2400, and 1850 (NH–HCl), 1478 and 1442 (C=C), and 687 cm^{-1} (CCl); mass spectrum (70 eV) *m/e* (rel intensity) 384 (100) and 307 (27).

Anal. Calcd for $C_{28}H_{21}ClN_2 \cdot HCl$: C, 73.52; H, 4.85; N, 6.13. Found: C, 73.50; H, 4.97; N, 6.20.

3,5-Diphenyl-4-benzhydrylidene-4*H*-pyrazole (49). A cooled solution (−78°) of 6 g (0.013 mol) of 3,5-diphenyl-4-chlorodiphenylmethylpyrazole hydrochloride in 200 ml of anhydrous tetrahydrofuran was treated with 2.6 g (0.026 mol) of triethylamine. The mixture was stirred for 10 min and then diluted with isooctane and the solid which formed was removed by filtration at −78° to yield 3.6 g (100%) of triethylamine hydrochloride. The resulting red solution was allowed to warm to 30° and concentrated *in vacuo* until red, needle-like crystals began to separate. The crystals were removed by filtration to give 4.7 g (94%) of **49**: mp 155–156°; λ_{max} (THF) 382 nm; ir ($CHCl_3$) 1540 (C=C), 1468 (C=C), 1448 (C=C), 1120, and 700 cm^{-1}; nmr ($CDCl_3$) δ 7.55–6.81 (m, 20 H); mass spectrum (70 eV) *m/e* (rel intensity) 386 (34), 385 (100), 384 (49), and 307 (26).

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.26; H, 5.10; N, 7.13.

3,5-Diphenyl-4-methoxydiphenylmethylpyrazole. To 10 ml of

anhydrous methanol was added 0.1 g (0.00026 mol) of the fulvene **49**, resulting in an immediate color discharge. Upon standing for 1 hr the solution began to deposit colorless plates which were removed by filtration to give 0.11 g (100%) of the ether: mp 105° (resolidifies and then melts at 170–172° dec); ir ($CHCl_3$) 3442 (NH) and 1078 cm^{-1} (COC); nmr ($CDCl_3$) δ 7.47–6.84 (m, 20 H) and 3.20 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 416 (25), 385 (100), and 339 (15).

Anal. Calcd for $C_{29}H_{24}N_2O$: C, 83.62; H, 5.81; N, 6.73. Found: C, 83.60; H, 5.76; N, 6.59.

3,5-Diphenyl-4-aminodiphenylmethylpyrazole. A chilled solution (5°) of 0.1 g (0.00026 mol) of the azafulvene **49** in 10 ml of anhydrous tetrahydrofuran was saturated with ammonia. The resulting colorless solution was evaporated *in vacuo* and the residue obtained was recrystallized from ether–hexane to give 0.097 g (93%) of the amine: mp 180–182°; ir ($CHCl_3$) 3442 (NH_2) and 3190 cm^{-1} (broad NH); nmr ($CDCl_3$) δ 7.32 (s, 2 H), 7.21 (s, 1 H), and 7.18–6.84 (m, 20 H); mass spectrum (70 eV) *m/e* (rel intensity) 401 (5), 387 (100), 386 (100), 220 (31), and 181 (25).

Anal. Calcd for $C_{28}H_{23}N_3$: C, 83.76; H, 5.77; N, 10.47. Found: C, 83.55; H, 5.53; N, 10.68.

3,4,α,α-Tetraphenylpyrazole-5-methanol (44). To a solution of phenyllithium (0.35 mol, prepared as above) in 500 ml of ether was added 27.8 g (0.1 mol) of solid methyl 3,4-diphenylpyrazole-5-carboxylate.[29] After the initial exothermic reaction was complete, the mixture was refluxed for 3 hr, then stirred for 18 hr at 30°. The reaction mixture was decomposed by the addition of 100 ml of saturated aqueous ammonium chloride solution and the ether layer after drying ($MgSO_4$) was evaporated *in vacuo* to give 39 g (97%) of **44**: mp 150–151°; ir (KBr) 3558 (OH), 3448 (NH), 1492 (C=C), 1450 (C=C), and 700 cm^{-1}; nmr ($CDCl_3$) δ 7.46–7.01 (m, 20 H); mass spectrum (70 eV) *m/e* (rel intensity) 402 (31), 384 (100), 325 (23), and 380 (18).

Anal. Calcd for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96. Found: C, 83.47; H, 5.53; N, 6.93.

3,4-Diphenyl-5-chlorodiphenylmethylpyrazole Hydrochloride. A suspension of 12 g (0.03 mol) of the alcohol **44** in 300 ml of anhydrous ether was saturated with dry hydrogen chloride. During the addition there was complete solution followed by the formation of a heavy precipitate. The mixture was stirred for 30 min, the solvent was evaporated *in vacuo*, and the residue was treated with a solution of 15 ml of thionyl chloride in 30 ml of dry benzene. After heating at reflux for 0.5 hr the resulting solution was stirred at 30° for 18 hr. Upon diluting with ether (200 ml), a precipitate formed which was removed by filtration and dried *in vacuo* to give 13.4 g (98%) of the salt, mp 131–133°. Two recrystallizations from tetrahydrofuran–ether afforded the analytical sample: mp 134–136°; ir (KBr) 3058 and 2400 (NH^+), 1573 (C=C), 1478 (C=C), 1442, and 683 cm^{-1} (CCl); mass spectrum (70 eV) *m/e* (rel intensity) 384 (100).

Anal. Calcd for $C_{28}H_{21}ClN_2 \cdot HCl$: C, 73.52; H, 4.85; N, 6.13. Found: C, 73.64; H, 5.02; N, 5.97.

3,4-Diphenyl-5-benzhydrylidene-5*H*-pyrazole (47). To a chilled solution (5°) of 4.57 g (0.01 mol) of 3,4-diphenyl-5-chlorodiphenylmethylpyrazole hydrochloride in 250 ml of anhydrous tetrahydrofuran was added 2.02 g (0.02 mol) of triethylamine. An intense red solution formed during the addition of the second equivalent of triethylamine. The reaction mixture was stirred for 5 min at 5°, then warmed to 30°, and the solvent was evaporated *in vacuo*. The resulting residue was dissolved in benzene and filtered through Celite under a dry nitrogen atmosphere to remove the triethylamine hydrochloride. The filtrate was concentrated *in vacuo* and diluted with *n*-hexane. Red, needle-like crystals formed which were removed by filtration and dried *in vacuo* to give 3.6 g (94%) of **47**. Upon heating, the crystals turned to a white solid at 120–130° which then melted at 179–181° (an ir of the white solid showed it to be identical with **50**). **47** had λ_{max} (THF) 393 nm; ir ($CHCl_3$) 1543, 1463, and 1452 (C=C), 1134, and 698 cm^{-1}; nmr ($CDCl_3$) δ 7.74–6.91 (m, 20 H); mass spectrum (70 eV) *m/e* (rel intensity) 385 (100), 384 (73), and 307 (34).

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.42; H, 5.22; N, 7.44.

1,2,5,5,6,7,10,10-Octaphenyl-5*H*,10*H*-dipyrazolo[1,2-*a*:1′,2′-*d*]pyrazine (50). A solution of 1.12 g (0.00024 mol) of 3,4-diphenyl-5-chlorodiphenylmethylpyrazole hydrochloride in 100 ml of dry tetrahydrofuran was cooled to 5° and treated with 0.495 g (0.0048 mol) of triethylamine. The mixture was stirred at room temperature for an additional 18 hr, during which time the intense red color faded. The triethylamine hydrochloride was removed by filtration (0.638 g, 96%). The filtrate was concentrated *in vacuo* and the residue was chromatographed over 30 g of Florisil. Elution with benzene afforded 0.741 g (75%) of **50**: mp 179–181°; ir ($CHCl_3$) 1623 (C=N), 1605 (C=C), 1475 (C=C), and 700 cm^{-1}; nmr ($CDCl_3$) δ 7.64–6.68 (m, 40 H); mass spectrum (70 eV) *m/e* (rel intensity) 768 (100) and 384 (27).

Anal. Calcd for $C_{56}H_{40}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.24; H, 5.37; N, 7.14.

Attempted Photolysis of 49. To a chilled solution (5°) of 2.29 g (0.0005 mol) of 3,5-diphenyl-4-chlorodiphenylmethylpyrazole hydrochloride in 150 ml of dry tetrahydrofuran was added 1.01 g (0.01 mol) of triethylamine. The red solution was diluted with 150 ml of cold tetrahydrofuran and photolyzed for 6 hr at 5° using a 450-W Hanovia high-pressure mercury discharge lamp in a Pyrex probe. Tlc indicated no reaction and the red color still persisted.

Photolysis of 47. To a chilled solution (5°) of 4.57 g (0.01 mol) of 3,4-diphenyl-5-chlorodiphenylmethylpyrazole hydrochloride in 300 ml of dry tetrahydrofuran–benzene (1:1 v/v) was added 2.02 g (0.02 mol) of triethylamine. The reaction mixture was stirred for 5 min and filtered through Celite under a dry nitrogen atmosphere to remove triethylamine hydrochloride (2.32 g, 85%). The clear red solution was photolyzed at 5° using a quartz probe and a 450-W Hanovia high-pressure mercury discharge lamp. The color of the solution was discharged without noticeable gas evolution during 20 min, after which the solvent was evaporated *in vacuo* to give 3.11 g (81%) of **50**, mp 179–181°.[14]

α,α-Diphenyl-1*H*-phenanthro[9,10-*c*]pyrazole-3-methanol (46). To a stirred solution of 52.5 ml of phenyllithium (2.3 *M*) in 70:30 benzene–ether in 100 ml of anhydrous ether was added 11 g (0.04 mol) of solid methyl 3,4-diphenylenepyrazole-5-carboxylate.[31] After the addition was complete, the mixture was refluxed for 6 hr, stirred at 30° for 18 hr, and decomposed using 5% aqueous hydrochloric acid (125 ml). The organic layer was washed with water, dried ($MgSO_4$), and filtered and the solvent was evaporated *in vacuo* to give 14 g (87%) of **46**, mp 168–171°. Two recrystallizations from benzene afforded an analytical sample of **46**: mp 172–173°; ir (KBr) 3410 (OH) and 3160 cm^{-1} (NH); nmr (DMSO-d_6) δ 10.01–6.81 (m, 18 H); mass spectrum (70 eV) *m/e* (rel intensity) 400 (27) and 382 (100).

Anal. Calcd for $C_{28}H_{20}N_2O$: C, 83.97; H, 5.03; N, 7.00. Found: C, 83.78; H, 5.09; N, 6.90.

3-Chlorodiphenylmethyl-1*H*-phenanthro[9,10-*c*]pyrazole. To a stirred solution of 20 ml of thionyl chloride in 40 ml of benzene was added 12 g (0.03 mol) of the solid alcohol **46**. The mixture was stirred for 18 hr at 30° and then refluxed for 4 hr. The precipitate which formed was removed by filtration, washed with anhydrous ether, and dried *in vacuo* to give 12 g (88%) of the salt, mp 248–251°. Two recrystallizations from tetrahydrofuran–ether afforded a pure sample, mp 250–252°. An analytically pure sample could not be prepared, as the salt was very hydroscopic: ir (KBr) 3250 and 2500 (NH^+) and 790 cm^{-1} (CCl); mass spectrum (70 eV) *m/e* (rel intensity) 382 (100) and 305 (15).

Attempted Synthesis of 3-Benzhydrylidene-3*H*-phenanthro[9,10-*c*]pyrazole (48). To a solution of 2.28 g (0.005 mol) of 3-chlorodiphenylmethyl-1*H*-phenanthro[9,10-*c*]pyrazole in 400 ml of dry tetrahydrofuran–benzene (1:1 v/v) at −78° was added 1.01 g (0.01 mol) of triethylamine. The light orange solution faded after 20 min. The resulting colorless solution was filtered through Celite to remove 1.27 g (92%) of triethylamine hydrochloride and from the filtrate only 1.8 g (95%) of **46**, mp 172–173°,[14] could be isolated.

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Registry No.—**7a**, 40235-35-6; **7c**, 50561-42-7; **8a**, 50561-43-8; **8b**, 50561-44-9; **8c**, 50561-45-0; **9a**, 50561-43-8; **10**, 50561-47-2; **11**, 50561-48-3; **14**, 38345-37-8; **15**, 50561-50-7; **16**, 50561-51-8; **17b**, 40759-79-3; **17c**, 40759-80-6; **18b**, 40795-33-3; **19a**, 40759-87-3; **20**, 40759-81-7; **25b**, 35364-02-4; **26a**, 22514-82-5; **26b**, 24667-98-9; **27a**, 40759-84-0; **27b**, 40759-85-1; **30**, 50561-60-9; **35**, 50561-61-0; **43**, 39672-37-2; **44**, 50561-63-2; **45**, 50561-64-3; **46**, 50561-65-4; **47**, 50561-66-5; **49**, 50561-67-6; **50**, 50561-68-7; methyl *p*-chlorophenylpropiolate, 50561-69-8; ethyl 1,2,3-triazole-4(5)-carboxylate, 40594-98-7; triphenylcarbinol, 76-84-6; 3-phenyl-1,2,4-triazole, 3357-42-4; 1-benzyl-3,α,α-triphenyl-1,2,4-triazole-5-methanol, 50561-72-3; 4(5)-phenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride, 50561-73-4; 5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride, 50561-74-5; 4(5)-*p*-chlorophenyl-5(4)-chlorodiphenylmethyl-1,2,3-triazole hydrochloride, 50561-75-6; 3(5)-chlorodiphenylmethyl-1,2,4-triazole hydrochloride, 50561-76-7; 3(5)-phenyl-5(3)-chlorodiphenylmethyl-1,2,4-triazole hydrochloride,

50561-77-8; 3(5)-phenyl-5(3)-methoxydiphenylmethyl-1,2,4-triazole, 50561-78-9; 4(5)-phenyl-5(4)-diphenylpiperidinomethyl-1,2,3-triazole, 50561-79-0; 4(5)-phenyl-5(4)-methoxydiphenylmethyl-1,2,3-triazole, 40759-82-8; pentaphenylpyridine, 40249-26-1; 2-*p*-chlorophenyl-3-phenylquinoline-4-carboxylic acid, 50561-82-5; methyl 3,5-diphenylpyrazole-4-carboxylate, 50561-83-6; 3,5-diphenyl-4-chlorodiphenylmethylpyrazole hydrochloride, 50561-84-7; 3,5-diphenyl-4-methoxydiphenylmethylpyrazole, 50561-85-8; 3,5-diphenyl-4-aminodiphenylmethylpyrazole, 50561-86-9; methyl 3,4-diphenylpyrazole-5-carboxylate, 50561-87-0; 3,4-diphenyl-5-chlorodiphenylmethylpyrazole hydrochloride, 50561-88-1; 3-chlorodiphenylmethyl-1*H*-phenanthro[9,10-*c*]pyrazole, 50561-89-2.

References and Notes

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Reaction of Oxaziridine with Heterocumulene. A Ketene, Isocyanates, and a Carbodiimide

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Reactions of oxaziridines **1** with a ketene, isocyanates, and a carbodiimide are studied, and the results are quite different from those of oxiranes, aziridines, or thiiranes. With diphenylketene (**2**), 2-*n*-alkyl- or *sec*-alkyloxaziridines give 3-alkyl-5,5-diphenyl-2-diphenylmethylidene-1,3-oxazolidin-4-ones (**3**), but 2-*tert*-butyloxaziridine **1f** rearranges to *N*-*tert*-butylbenzamide. In the reactions with isocyanates, cycloadditions forming 1,2,4-oxadiazolidin-5-ones **10** are exclusively observed. The reactions similar to that with the ketene **2** occur between 2-*n*-alkyloxaziridines and diphenylcarbodiimide, giving hexahydro-1,3,5-triazine derivatives **17** as a result of hydride shift. The oxaziridine **1f** undergoes 1:1 cycloaddition with the carbodiimide.

Many reactions of three-membered heterocycles containing one heteroatom with heterocumulenes have been reported. Oxiranes react with a ketene, an isocyanate, and a carbodiimide to give dioxolans[1] or γ-lactones,[2] oxazolidinones,[3] and imidazolidinones,[1] respectively; imidazolidinones are also given by the cycloaddition of aziridines to an isocyanate.[4] Thiiranes react with a ketene to afford thiolactones.[5]

On the other hand, the chemistry of three-membered rings containing two heteroatoms has not been so widely studied. In particular, there has been no report on the cycloadditions of such heterocycles to heterocumulenes.

In this study, the reactions of oxaziridines with a ketene, isocyanates, and a carbodiimide are presented. The accompanying report[6] describes the reactions of oxaziridines with sulfur-containing heterocumulenes.