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(44) A sample of methyl 4-iodocrotonate was prepared in the following fashion. To a solution containing 20.5 g of methyl crotonate in 110 mL of carbon tetrachloride was added 29.1 g of *N*-bromosuccinimide and 100 mg of dibenzoyl peroxide. The mixture was heated at reflux for 48 h, filtered, and concentrated under reduced pressure. The resulting liquid was distilled at 92–95 °C (10 mm) to give 23 g of methyl 4-bromocrotonate. To a solution containing 9.0 g of this material in 300 mL of dry acetone was added 12 g of sodium iodide. The mixture was stirred at room temperaure for 20 h. A normal workup procedure gave a 93% yield of methyl 4-iodocrotonate.

Intramolecular Cyclization of Nitrile Imines. Synthesis of Indazoles, Fluorenes, and Aza Analogues[1a]

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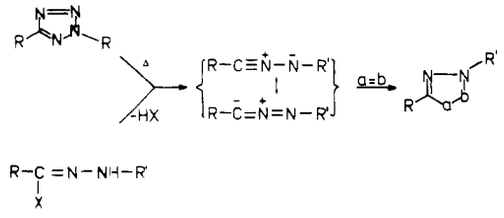
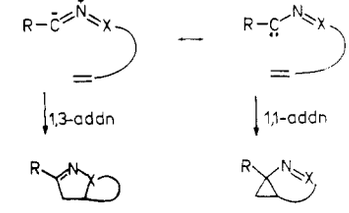
Received November 16, 1977

Flash thermolysis of 2,5-diaryltetrazoles **2** at 400–500 °C (10^{-3} mm) gives 3-arylindazoles **5** in yields of 96–100%. Thus, 2,5-diphenyl-, 2-(*p*-tolyl)-5-phenyl-, 2-phenyl-5-(*p*-tolyl)-, 2,5-di(*p*-tolyl)-, and 2-phenyl-5-(4-pyridyl)tetrazole furnish 3-phenyl-, 3-phenyl-5-methyl-, 3-(*p*-tolyl)-, 3-(*p*-tolyl)-5-methyl-, and 3-(4-pyridyl)indazole, respectively. Indazoles **5** are formed also by heating the tetrazoles **2** in tetralin at 207 °C for 15 min. Flash thermolysis of the same tetrazoles **2** at 800 °C (10^{-3} mm) gives 2,6-disubstituted fluorenes **7** (2,6 substituents = H or CH_3) or 3-azafluorene (**7e**) in yields of 90–100%. The thermolysis of 3-phenylpyrazolo[3,4-*b*]pyridine (**8**) at 770 °C resulted in a 49% conversion to 4-azafluorene (**9**). Thermolysis of 2,4-diphenyl-1,3,4-oxadiazolin-5-one (**16a**) at 500 °C (10^{-2} mm) gave 3-phenylindazole (94%); at 750 °C fluorene was obtained (84%). 2-Methyl-4-phenyl-1,3,4-oxadiazolin-5-one (**16b**) gave at 450 °C 3-methylindazole (89%) and at 650 °C styrene (94%). The results are interpreted in terms of the intermediate formation of nitrile imines by loss of N_2 from **2** and of CO_2 from **16**. The nitrile imines are regarded as a resonance hybrid of bent dipolar and carbene structures (**23**) which cyclize unto the remote aromatic ring.

The cycloaddition of 1,3 dipoles has become an important method for the synthesis of five-membered heterocyclic rings.[2] For example, nitrile imines generated by the thermal decomposition[3a] of 2,5-disubstituted tetrazoles[3c] or by base-induced elimination from hydrazonyl halides[3b] undergo in situ addition to acetylenes, olefins, and nitriles, yielding pyrazole



or triazole derivatives.[2] The cycloaddition of 1,3 dipoles can also take place intramolecularly to suitably oriented dipolarophiles.[4] Recently, it has been shown that intramolecular 1,1 addition of nitrile ylides[4,5] as well as nitrile imines[6] can compete with the normal 1,3 addition when certain geometric constraints are imposed. In these cases, the reactions can be formulated in terms of the carbene forms of the dipoles.[4,5]



Huisgen[2] recognized carbene forms as resonance structures of 1,3 dipoles; however, such species may exist in two distinct molecular geometries: a bent carbene-like structure and/or a linear dipolar structure.[7] The ab initio STO-3G and 4–31G

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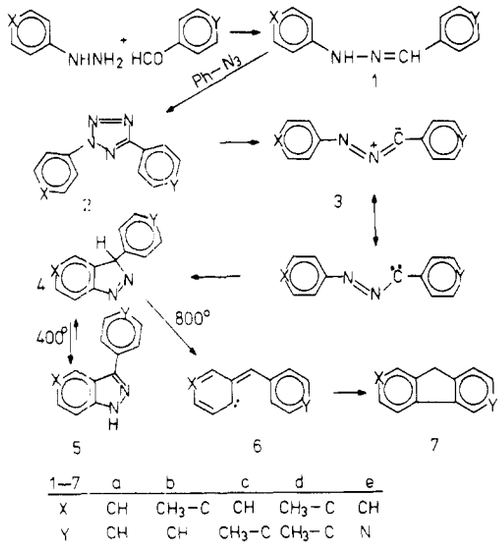
Scheme I



1–7	a	b	c	d	e
X	CH	CH_3–C	CH	CH_3–C	CH
Y	CH	CH	CH_3–C	CH_3–C	N

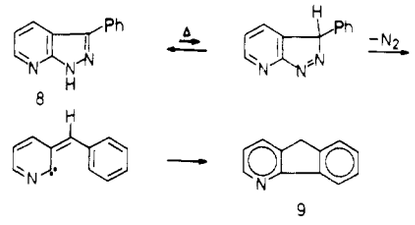
calculations of Houk and Caramella[7b] suggest that the nitrile imine, in particular, is a flexible molecule which can adapt its geometry according to the nature of the reaction; thus, electrophilic reagents would favor a planar structure possessing a relatively high-lying HOMO, whereas nucleophilic reagents would promote the bent carbene-like form, which possesses a low-lying LUMO.

In this paper we wish to report a fundamentally new type of reaction of 1,3 dipoles, namely, intramolecular ring closure of nitrile imines unto aromatic rings. The nitrile imines were generated by thermolysis of 2,5-disubstituted tetrazoles or by a new procedure employing 1,3,4-oxadiazolin-5-ones. The results are of importance with respect to the carbenic nature of 1,3 dipoles.[8]

Results and Discussion

Using the procedure of Dimroth and Merzbacher[9,10] the required 2,5-diaryltetrazoles **2** were prepared by treatment of the hydrazones **1** with phenyl azide (Scheme I). Flash thermolysis of the tetrazoles at 400–500 °C gave near quantitative yields of 3-arylindazoles **5** (Scheme I, Table I). The

Scheme II



substituent pattern in **5** demonstrates that the carbon atom of the nitrile imine **3** becomes bonded to the aromatic ring originating from the arylhydrazine. This would lead initially to the 3*H*-indazoles **4**. When the temperature is high enough (ca. 800 °C) the 3*H*-indazoles may eliminate a further molecule of N_2, leading to the carbenes **6**, which cyclize to 2,6-disubstituted fluorenes **7**, again in near quantitative yields (Table I). The 3*H*-indazoles may also be populated by direct thermal excitation of the 1*H*-indazoles **5**. However, since **4** is an energetically very unfavorable tautomer, yields of fluorene are far from quantitative when starting from **5**. This circumstance in itself supports the assumption of an initial formation of the unfavorable tautomer **4** in the thermolysis of the tetrazoles **2**.

As an example of fluorene formation from indazoles, the known 3-phenylpyrazolo[3,4-*b*]pyridine[11] (**8**) was thermolyzed at 770 °C, resulting in a 49% conversion to 4-azafluorene (**9**) (Scheme II), the remainder of the starting material being recovered. It has been reported[12] that indazoles and pyrazolo[3,4-*b*]pyridines may also yield arylcarbenes by gas-phase thermolysis. This contention has been criticized[13] and can be excluded in the present reaction since it is known[14] that the arylcarbene **10** furnishes a mixture of 1- and 3-azafluorene (**11** and **12**) and not 4-azafluorene (**9**) when generated from the diazo compound **13**.

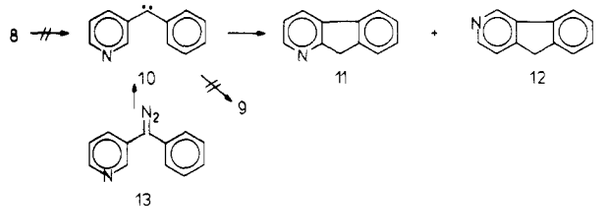
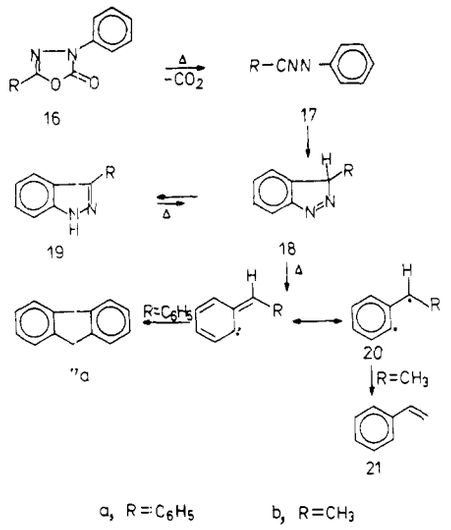


Table I. Thermolysis of 2,5-Diaryltetrazoles 2

			Yield of products, %			
Registry no.	Tetrazole	Conditions[a]	5	Registry no.	7	Registry no.
18039-45-7	**2a**	$420/10^{-3}$	100[b]	13097-01-3		
		$515/10^{-3}$–10^{-2}	92[b]		5[c]	86-73-7
		$800/10^{-2}$			95[c]	
		Tetralin, reflux 15 min	78[b]			
20433-19-6	**2b**	$515/10^{-3}$	100[d]	57614-16-1		
		$800/10^{-3}$			95[e]	1430-97-3
20433-11-8	**2c**	$515/10^{-3}$	96[f]	65452-73-5		
		$800/10^{-3}$			100[g]	2523-39-9
59635-32-4	**2d**	$500/10^{-3}$	98[h]	65452-74-6		
		$800/10^{-3}$			96[i]	65452-75-7
65452-72-4	**2e**	$500/10^{-3}$	99[j]	37885-56-6		
		$800/10^{-3}$			90[k]	244-42-8
		Tetralin, reflux 15 min	64[j]			

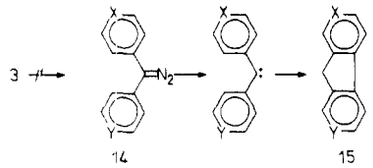
[a] Gas-phase thermolyses used apparatus A (see Experimental Section), and conditions are expressed as temperature (°C)/pressure (mm). [b] 3-Phenylindazole, mp 115–116 °C (from hexane) [lit. mp 115–116 °C: W. Borsche and W. Scriba, *Justus Liebigs Ann. Chem.*, **540**, 83 (1939)]. [c] Fluorene, mp 115–116 °C (identical with an authentic sample). [d] 5-Methyl-3-phenylindazole (see Experimental Section). [e] 2-Methylfluorene, mp 104–105 °C [lit. mp 104–105 °C: *Beilsteins Handbuch der Org. Chem.*, **5**, III, 1991 (1964)]. [f] 3-(*p*-Tolyl)indazole (see Experimental Section). [g] 3-Methylfluorene, mp 88–89 °C [lit. mp 88–90 °C: *Beilsteins Handbuch der Org. Chem.*, **5**, III, 1992 (1964)]. [h] 5-Methyl-3-(*p*-tolyl)indazole (see Experimental Section). [i] 2,6-Dimethylfluorene, mp 65–66 °C (sublimed at 25 °C (0.1 mm)) [lit. mp 66–67 °C: *Beilsteins Handbuch der Org. Chem.*, **5**, III, 2006 (1964)]. [j] 3-(4-Pyridyl)indazole (see Experimental Section). [k] 3-Azafluorene (see Experimental Section).

Scheme III

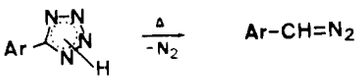


a, R = C_6H_5 b, R = CH_3

It can also be excluded that the fluorenes **7** (Scheme I) arise via a rearrangement of the nitrile imines **3** to diaryldiazomethanes **14.** The latter are known to give 2,7-disubstituted fluorenes **15** via a double carbene–carbene rearrangement.[15]



The elimination of this pathway was particularly important because 5-aryltetrazoles do decompose thermally to aryldiazomethanes; a hydrogen shift is involved in these reactions.[8c]

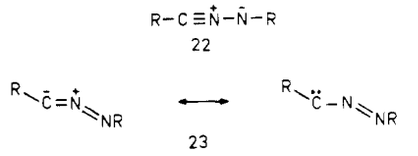


Furthermore, there is some evidence that the parent nitrile imine (isodiazomethane) tautomerizes to diazomethane.[16]

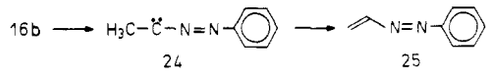
The cyclization of nitrile imines to indazoles is not limited to the gas phase. The tetrazoles **2a** and **2e** were decomposed in the liquid phase, i.e., under conditions where the nitrile imines **3** can be trapped[3] by added dipolarophiles. In the absence of trapping agents, the corresponding indazoles were formed in considerable yields (Table I). Thus, the ability to undergo intramolecular cyclization may be assumed to be a basic property of such 1,3 dipoles.

In order to widen the scope of nitrile imine chemistry, a new precursor was sought. 1,3,4-Oxadiazolin-5-ones **16** are easily accessible from acid hydrazides[17] but have received relatively little attention. The gas-phase thermolyses of oxadiazolinones **16a,b** (Scheme III) are reported in Table II. The reactivity of **16a** is very similar to that of **2a,** leading to high yields of 3-phenylindazole (**19a**) or fluorene (**7a**), depending on the temperature. Similarly, **16b** gives rise to 3-methylindazole (**19b**) in the low temperature range. At higher temperatures, the carbene or diradical **20** isomerizes to styrene (**21**) in near quantitative yield, as has also been observed in the thermolysis of 3-methylindazole itself.[12a,b]

Consider now the mechanism of cyclization of the nitrile imines, **3** → **4** and **17** → **18.** Recent theoretical[7] and experimental[5] work indicates that nitrilium betaines may exist in linear and/or bent forms, of which the latter was found to be the ground state in the case of nitrile ylides.[7b] The related forms of a nitrile imine can be represented in valence bond terms by **22** and **23.**



The requirement of a bent geometry in the transition state leading to **4** and **18** (Schemes I and III) rules out the linear structure **22** but does not, of course, say anything about the ground-state geometry of the species. The bent, carbene-like nitrile imines **23** nicely rationalize the cyclizations as carbene-type reactions. The finer details may involve electrocyclization, electrophilic substitution, or CH insertion by the carbenic carbon. The results obtained with **16b** are particularly important in this respect for they indicate that the reactive intermediate should not be regarded as a pure carbene. Had such a species (**24**) been formed, we would expect a very rapid rearrangement to the azo olefin **25.** Although **25** could



give rise to modest yields of styrene, it cannot account for the virtually quantitative formation of 3-methylindazole.

The 1,2-hydrogen shift in alkylcarbenes is exceedingly fast,[18] competing strongly with all other carbene reactions. However, the bent carbene-like nitrile imine **23** differs from an ordinary singlet carbene in that it is the *second* lowest unoccupied molecular orbital (SLUMO) which possesses a large coefficient at the carbenic carbon atom.[7b] The propensity of **23** toward 1,2-hydrogen shifts may, therefore, be overridden by the interaction with the aromatic ring bonded to N, which can, in principle, overlap simultaneously with the HOMO and the SLUMO of **23.**[14]

The optimized STO-3G geometry of **23** (R = H) resembles a trans azo compound.[7b] In the cyclizations leading to indazoles (**4** and **18**) a geometrical isomerization to the cis azo forms of **23** (R = aryl) is required. The calculated flexibility[7b] of the molecule is expected to facilitate this process.

In conclusion, the hybrid of carbenic and dipolar bent structures (**23**) best describes the nitrile imines involved in the cyclization reactions reported here. These reactions have considerable potential for the synthesis of indazoles and fluorenes since a variety of starting materials **2** and **16** can be prepared from simple chemicals.[17c,19] As an example, 3-azafluorene was prepared previously in 12% overall yield in a lengthy synthesis;[14] it can be obtained in higher yield but as a mixture with 1-azafluorene via a carbene–carbene rearrangement starting with phenyl-3-pyridyldiazomethane

Table II. Thermolysis of 1,3,4-Oxadiazolin-5-ones 16

Registry no.	Oxadiazolone	Conditions[a]	Product, yield	Registry no.
19226-10-9	**16a**	$500/10^{-2}$	3-Phenylindazole (**19a**), 94%	13097-01-3
		$750/10^{-2}$	Fluorene (**7a**), 84%[b]	
28740-63-3	**16b**	$450/10^{-2}$	3-Methylindazole (**19b**), 89%	3176-62-3
		650.10^{-2}	Styrene (**21**), 94%	100-42-5

[a] Apparatus B was used (see Experimental Section), and conditions are expressed as temperature (°C)/pressure (mm). [b] An 8.6% yield of 9,9′-bifluorenyl was also obtained; this is most probably a secondary pyrolysis product of fluorene.

(13).[14] However, 3-azafluorene is a highly unstable compound, rapidly turning blue and later black at room temperature. It is therefore impossible to obtain reasonable yields of this compound unless it is the only reaction product. This requirement is satisfied in the thermolysis of **2e** at 800 °C (Table I).

Experimental Section

General. Two pyrolysis apparatuses were used. Apparatus A employed a 30 × 2 cm quartz tube evacuated with an Edwards "Diffstak," capable of an ultimate vacuum of ca. 10^{-7} mm. Apparatus B consisted of a 40 × 3.5 cm quartz tube, the pump giving an ultimate vacuum of ca. 10^{-3} mm. Further details of the procedure have been published elsewhere.[20] Samples were in all cases sublimed into the pyrolysis tube below their melting points. The products were collected in a trap cooled in liquid N_2 or dry ice–acetone. The pressures recorded during pyrolysis are those of gases escaping the traps. The products were often spectroscopically pure or else they were purified by sublimation or recrystallization. When mixtures of indazoles and fluorenes were obtained, they were readily separable by thin-layer and column chromatography on SiO_2, eluting the fluorene first with $CHCl_3$ and then the indazole with $CHCl_3$–MeOH (9:1).

Mass spectra were recorded on a CEC 21-490 instrument at 70 eV using a direct inlet at a source temperature of 200 °C and are reported as *m/e* values followed by relative abundance (percent of base peak). Melting points are corrected. Microanalyses were performed by Mr. E. Thommen, Universität Basel, Basel, Switz.

2-(*p*-Tolyl)-5-phenyltetrazole (2b). To a solution of 0.545 g (23.7 mmol) of Na in 12 mL of 2-methoxyethanol was added 2.1 g (10 mmol) of benzaldehyde *p*-tolylhydrazone and 1.23 g (10.34 mmol) of phenyl azide. The mixture was stirred magnetically at 100 °C for 14 h, cooled, and diluted with 10 mL of EtOH, after which the product crystallized: 1.37 g (58%) (lit.[10] 19.2%); mp 102–103 °C (lit.[10] mp 103–104 °C).

2,5-Di(*p*-tolyl)tetrazole (2d). To a solution of 0.476 g (20.7 mmol) of Na in 10 mL of 2-methoxyethanol was added 1.97 g (8.79 mmol) of *p*-tolualdehyde *p*-tolylhydrazone and 1.08 g (9.08 mmol) of phenyl azide. The mixture was refluxed (124 °C) for 7 h, cooled, diluted with 10 mL of EtOH, and allowed to crystallize, yielding 1.14 g (52%). Recrystallization from EtOH furnished colorless needles: mp 139 °C (lit.[19a] mp 139–140 °C); mass spectrum, *m/e* 250 (M^+, 12), 222 (40), 118 (4), 117 (3), 116 (3), 105 (100), 104 (23), 78 (20). Anal. Calcd for $C_{15}H_{14}N_4$: C, 71.98; H, 5.64; N, 22.38. Found: C, 71.70; H, 5.59; N, 22.44.

2-Phenyl-5-(4-pyridyl)tetrazole (2e) was obtained in 81% yield following the above procedure. After recrystallization from ethanol it had mp 141.5–142.5 °C; mass spectrum, *m/e* 223 (M^+, 3), 195 (29), 105 (0.1), 104 (0.1), 91 (100), 77 (0.3), 64 (2), 51 (0.5). Anal. Calcd for $C_{12}H_9N_5$: C, 64.56; H, 4.06; N, 31.37. Found: C, 64.64; H, 3.99; N, 31.40.

Gas-phase pyrolysis of tetrazoles 2 was carried out using apparatus A. Conditions and yields are collected in Table I. Known compounds were identified by TLC and spectral comparison with authentic materials. The following examples are typical.

3-Phenyl-5-methylindazole (5b). 2b (987 mg, 4.22 mmol) was thermolyzed at 515 °C (10^{-3} mm), being sublimed in at 90–100 °C. 3-Phenyl-5-methylindazole (977 mg, 100%) deposited outside the pyrolysis tube. An analytical sample was obtained by recrystallization from ethyl acetate–petroleum ether (bp 40–60 °C): mp 117–118 °C; NMR (CD_3OD) δ 7.8–6.8 (m, 8 H), 2.1 (s, 3 H); IR (KBr) 3150 broad s, 3040 s, 2920 s, 1620 w, 1500 s, 1450 m, 1330 s, 1310 m, 1260 m, 1110 s, 990 s, 940 m, 780 s, 750 s, 700 s cm^{-1}; mass spectrum, *m/e* 208 (M^+, 100), 207 (28), 131 (6), 104 (13), 77 (18). Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.52; H, 5.85; N, 13.40.

3-(*p*-Tolyl)indazole (5c) was prepared in 96% yield from **2c** in a similar manner: mp 95–96 °C (lit.[21] mp 97–98 °C); NMR (CCl_4) δ 7.95 (d, *J* = 8 Hz, 2 H, superimposed on unresolved peaks, 1 H), 7.30 (d, *J* = 8 Hz, 2 H), 7.3–6.6 (m, 3 H), 2.38 (s, 3 H); IR (KBr) 3150–3000 broad s, 2960–2850 broad s, 1630 s, 1485 s, 1345 s, 1260 s, 1110 s, 1010 s, 995 s, 910 s, 825 s, 780 s, 740 s cm^{-1}; mass spectrum, *m/e* 208 (M^+, 100), 104 (M^{2+}, 5), 91 (8).

3-(*p*-Tolyl)-5-methylindazole (5d) was obtained by pyrolysis of **2d** (Table I). An analytical sample was obtained by recrystallization from ethyl acetate–petroleum ether followed by sublimation: mp 120 °C; NMR (CCl_4) δ 8.0 (d, *J* = 8 Hz, 2 H, C-2′ and C-6′), 7.75 (broadened s, 1 H, C-4), 7.35 (d, *J* = 8 Hz, 2 H, C-3′ and C-5′), 6.95 (center, distorted AB pattern, 2 H, C-6 and C-7), 2.45 (s, 6 H, CH_3); IR (KBr) 3130 broad s, 2960 s, 1630 w, 1490 s, 1440 m, 1320 s, 1305 m, 1260 m, 1180 w, 1155 w, 1105 s, 985 s, 940 s, 825 s, 795 s cm^{-1}; mass spectrum, *m/e* 222 (M^+, 100), 111 (6), 110 (5), 91 (6). Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.82; H, 6.39; N, 12.59.

3-(4-Pyridyl)indazole (5e) was prepared by pyrolysis of **2e** (Table I): mp 188 °C (from 2-propanol); NMR (acetone-d_6) δ 8.2 (d, *J* ≅ 6 Hz, 2 H), 7.5 (d, *J* ≅ 6 Hz, 2 H), 7.8–6.6 (m, ~4 H); IR (KBr) 3050 broad s, 2850 broad s, 1600 s, 1470 m, 1410 m, 1360 m, 1345 s, 1310 m, 1255 s, 1220 m, 1110 w, 1060 w, 1010 s, 990 s, 900 m, 825 s, 730 s, 610 s cm^{-1}; mass spectrum, *m/e* 195 (M^+, 100), 168 (5), 118 (6), 97.5 (M^{2+}, 3), 98 (3), 78 (3), 51 (4). Anal. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.58; H, 4.61; N, 21.42.

3-Azafluorene (7e). 2e (400 mg, 1.79 mmol) was pyrolyzed at 800 °C (10^{-3} mm) for 3 h, the sample being sublimed into the apparatus at 100–125 °C. The product, a yellow oil (270 mg, 90%), was taken up in ether and rapidly chromatographed on SiO_2–chloroform, the yellow band being collected under N_2. Concentration afforded a 70% yield of pure **7e**, whose gas chromatographic and NMR, IR, and mass spectral properties were identical with those of an authentic sample.[14] The compound turns blue–green very rapidly and deteriorates even under N_2 and in the cold.

4-Azafluorene (9). 3-Phenylpyrazolo[3,4-*b*]pyridine[11] (**8**) (500 mg) was pyrolyzed at 770 °C (10^{-3}–10^{-2} mm), being sublimed in at 115–120 °C in the course of 2.5 h. The product was chromatographed on SiO_2, eluting with chloroform to yield 217 mg of starting material (43%) and 210 mg (49%) of 4-azafluorene: mp 93–94 °C; mixture melting point with an authentic sample (Aldrich), 93–95 °C. The compound had spectral properties identical with those of the commercial sample.

Liquid-Phase Thermolysis of Tetrazoles. A solution of 111 mg (0.5 mmol) of 2,5-diphenyltetrazole (**2a**) in 50 mL of tetralin was added dropwise to 50 mL of refluxing tetralin (207 °C). Heating was continued for 15 min longer, after which time the solvent was removed in vacuo. From the residual brown solid 76 mg (78%) of 3-phenylindazole (**5a**) was sublimed at 100 °C (10^{-2} mm). The mixture melting point (115–116 °C) and IR and mass spectra were identical with those of authentic material.

In the same manner, a 64% yield of 3-(4-pyridyl)indazole (**5e**) was obtained from 2-phenyl-5-(4-pyridyl)tetrazole (**2e**). The product was identical with the one prepared by gas-phase thermolysis (vide supra).

Pyrolysis of oxadiazolinones was carried out using apparatus B. **2,4-Diphenyl-1,3,4-oxadiazolin-5-one**[17a] (**16a**; 500 mg, 2.1 mmol) was pyrolyzed at 500 °C (0.01 mm). The resulting slightly yellow product was recrystallized from petroleum ether to give 384 mg (94%) of 3-phenylindazole, identified by comparison with an authentic sample. The results of pyrolysis at higher temperatures are indicated in Table II.

2-Methyl-4-phenyl-1,3,4-oxadiazolin-5-one[17b] (**16b**; 500 mg, 2.8 mmol) was pyrolyzed at 450 °C (0.01 mm). The resulting slightly colored solid was chromatographed on SiO_2, eluting with ether–hexane (5:1) to give 331 mg (89%) of 3-methylindazole, mp 113 °C (lit.[22] mp 113 °C).

16b (500 mg, 2.8 mmol) was also pyrolyzed at 650 °C (0.01 mm). The liquid product was redistilled under high vacuum and identified as styrene by gas chromatography and NMR and IR spectroscopy, yield 274 mg (94%).

Acknowledgment. We gratefully acknowledge the financial support of this work by the Deutsche Forschungsgemeinschaft and the Schweizerischer Nationalfonds. Some of the early experiments were carried out by Messrs. J.-P. Jubin and J.-P. Hagenbuch (1975).

Registry No.—**1a,** 588-64-7; **1b,** 1858-99-7; **1c,** 2829-25-6; **1d,** 65452-76-8; **1e,** 7757-39-3; **8,** 65452-77-9; **9,** 244-99-5.

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Annelations of Amidines on Halonitroaromatics. A One-Step Route to Quinoxaline and Imidazoquinoxaline *N*-Oxides and Related Structures

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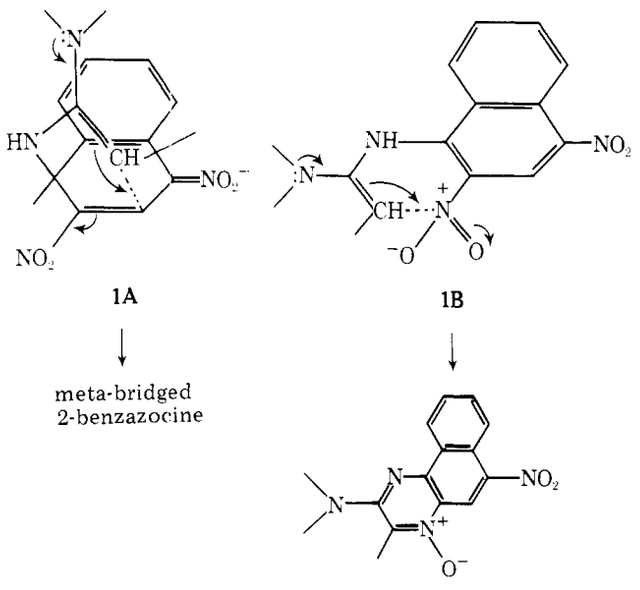
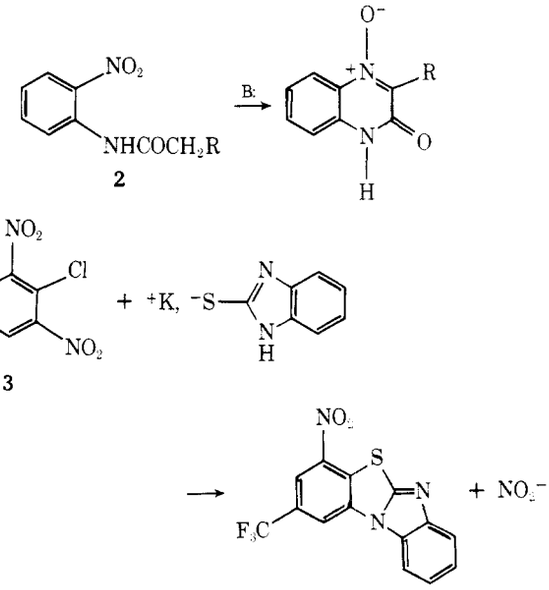
Received November 15, 1977

The reactions of α-phenylacetamidines with *o*-nitrohaloaromatics and related substrates have been shown to yield displacement–addition products in which the amidine is annelated across the ring carbon and nitrogen of an adjacent nitro group in the aromatic. The products are quinoxaline and imidazoquinoxaline *N*-oxides. The reactivity of amidines in meta-bridging reactions vs. ortho substituent annelations is discussed.

We have previously found that the nitrogen and α carbon of α-phenylacetamidines act as nucleophilic centers in meta-bridging reactions[1] (eq 1) of polynitrobenzenes, pyridines, and naphthalenes.[2-4] For example, reaction of α-phenyl-*N*,*N*-dimethylacetamidine with 1,3-dinitronaphthalene yields products in which a CCN moiety from the amidine is annelated across the 2 and 4 positions of the aromatic substrate.[3] The amidine in this reaction acts as a bifunctional nucleophile. Because of tetrahedral geometry at the C-1 carbon of anionic sigma complexes[5] we have previously proposed that geometrical constraints in the intermediate precursor to benzazocines (the addition complex **1A**) favor nucleophilic attack of amidine carbon at the 3 position in the cyclization step,[1,2] i.e.,



Consideration of geometry in a planar SnAr displacement "intermediate" **1B** (resulting from amidine attack on an aromatic bearing a good leaving group) led us to suppose that attack on an ortho substituent would be favored. This supposition is supported by the observed cyclization of nitroanilides like **2**.[6] *o*-Nitrite displacement could also occur, however, as observed in the reaction of **3** with 2-mercapto-



benzimidazole.[7] We have carried out reactions of several amidines with various 1-substituted 2-nitroaromatics in order to further explore patterns of amidine reactivity.

As noted above, while 1,3-dinitronaphthalene yields a 2-benzazocine with α-phenyl-*N*,*N*-dimethylacetamidine, 1-methoxy-2,4-dinitronaphthalene yields an entirely different

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