Nitrile Imine and Carbene Rearrangements. From Furfural to Benzofulvene-8-carboxaldehyde, 8-Benzofulvenylcarbene, and 1-Vinylideneindene

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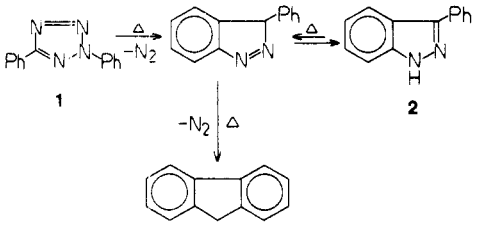
Flash vacuum pyrolysis of 2-phenyl-5-(2-furyl)tetrazole (4) at temperatures ≤400 °C yields 3-(2-furyl)indazole (7). At temperatures ≥400 °C, a rearrangement to benzofulvene-8-carboxaldehyde (10) takes place. Thermolysis of the sodium salt of the tosylhydrazone of 10 at 50 °C gives 1-(2-diazoethylidene)indene (14). Flash vacuum pyrolysis of 14 gives, at 400 °C, spiro[cyclopropene-1,1'-indene] (16), at 600 °C, 1*H*-cyclopent[*cd*]indene (18), and, at 800 °C, a 2:1 mixture of 18 and 1-vinylideneindene (19).

It was shown previously[1] that 2,5-diaryltetrazoles (1) decompose in the gas phase as well as in solution with formation of nitrile imines which cyclize to 3-arylindazoles (2). By flash pyrolysis of either 1 or 2 at higher temperatures (ca. 800 °C) a second molecule of N_2 is extruded, leading to the formation of fluorenes (3).



We now wish to report a deviation from this scheme, observed in 2-phenyl-5-(2-furyl)tetrazole, whereby a rearrangement to benzofulvene-8-carboxaldehyde (10) takes place. Reactions of the carbene (15) derived from this aldehyde are also described.

Results and Discussion

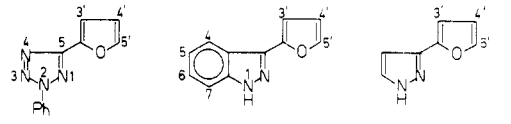
2-Phenyl-5-(2-furyl)tetrazole (4) was prepared from furfural in two steps as described by Ito et al.[2] Flash vacuum pyrolysis of the tetrazole 4 at 400 °C (10^{-3} torr) gave a 40% yield of 3-(2-furyl)indazole (7) and 18% of benzofulvene-8-carboxaldehyde (1-ethylideneinden-9-al) (10), together with small amounts of starting material and polymer.

A decrease of the pyrolysis temperature to 350 °C resulted in formation of the indazole 7 as the exclusive product, but at this temperature most of the starting material was recovered unchanged. An optimal yield of the aldehyde 10 was obtained at 720 °C (64%); at this temperature the indazole had disappeared entirely, but 24 wt % polymer was also formed.

The indazole 7 was identified on the basis of its spectra and elemental analysis. The ^1H NMR spectrum is particularly instructive, the pattern due to the furyl ring being almost identical with that in the tetrazole 4 and in 3-(2-furyl)pyrazole (11) (see Table I). The NMR spectrum of the latter compound has been analyzed by Gronowitz.[3]

The aldehyde 10 has been prepared previously in a different manner,[4] and it was identified by spectral data

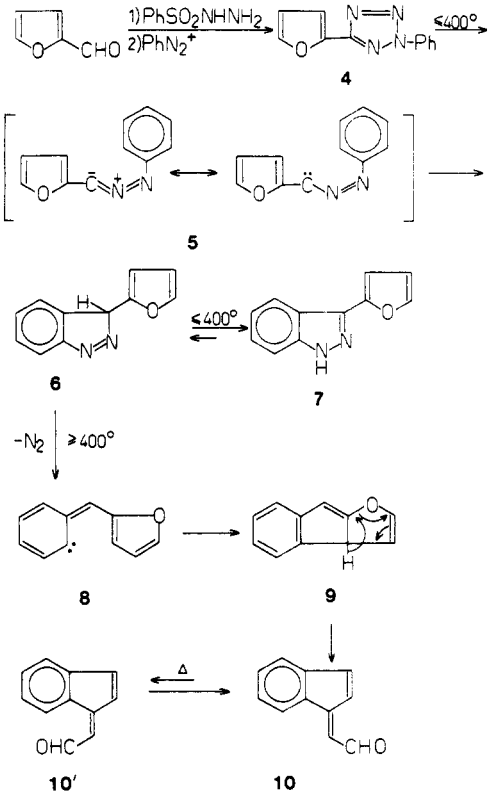
Table I. ^1H NMR Spectra of 2-Furyl Heterocycles[a]



proton	4	7	11
H-3'	6.50 (dd, J = 4 and 1)	6.25 (dd, J = 4 and 1)	6.77 (dd, J = 4 and 1)
H-4'	6.0 (dd, J = 4 and 2)	5.95 (dd, J = 4 and 2)	6.53 (dd, J = 4 and 2)
H-5'	7.05 (dd, J = 2 and 1)	7.05 (dd, J = 2 and 1)	7.6 (dd, J = 2 and 1)
H-1		12.3 (br, 1 H)	
aromatic	6.8-7.5 (m, 5 H)	6.5-7.5 (m, 4 H)	

[a] Spectra were recorded in acetone-d_6, except for H-1 in 7, which refers to $CDCl_3$ solution. Chemical shifts δ relative to tetramethylsilane; coupling constants (J) in hertz.

Scheme I



(see Experimental Section). The element =CH—CHO gives rise to two doublets (J = 8 Hz) at δ 6.76 and 10.40

(1) C. Wentrup, A. Damerius, and W. Reichen, *J. Org. Chem.*, **43**, 2037 (1978).
(2) S. Ito, Y. Tanaka, A. Kakehi, and K. Kondo, *Bull. Chem. Soc. Jpn.*, **49**, 1920 (1976).
(3) S. Gronowitz, *Acta Pharm. Suec.*, **5**, 167 (1968).
(4) T. Severin, R. Adam, and H. Lerche, *Chem. Ber.*, **108**, 1756 (1975).

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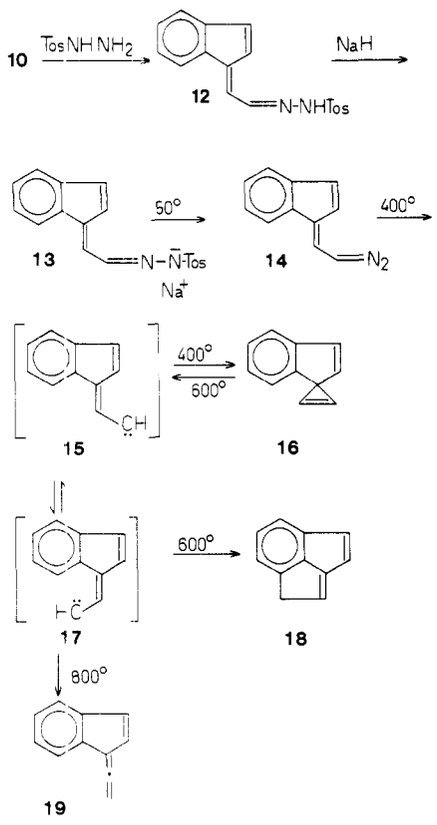
Scheme II

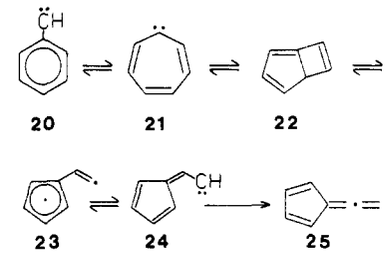


in the ^{1}H NMR spectrum. However, a second set of doublets ($J \simeq 8$ Hz) at δ 6.33 and 10.83 indicate the presence of the Z isomer, **10′**, with an E/Z ratio of **10:10′** $\simeq$ 9:1.

The pyrolysis results described above are interpreted mechanistically in Scheme I. Formation of the indazole **7** via the nitrile imine **5** is analogous to our previous results with diaryltetrazoles.[1] However, the temperature required for the loss of the second molecule of N_2 from the indazole is exceptionally low. This is thought to proceed via the 3*H*-indazole **6**, leading to the carbene **8**, the latter cyclizing to **9**. Instead of isomerizing to an indenofuran (cf. the formation[1] of **3** from **1** and **2**), **9** undergoes a 1,5-sigmatropic shift of hydrogen, followed by ring opening to give **10**. A somewhat related ring opening of a furan ring due to a carbene attack has been observed by Nwaji et al.[5] in the $CuSO_4$-catalyzed rearrangement of 1-diazo-4-furylbutan-2-one to 1-(1-propenyl)cyclopenten-3-on-3′-al.

The aldehyde **10** was used to generate benzofulvenylcarbene **15** as shown in Scheme II. Reaction with tosylhydrazine gave the hydrazone **12**, which with sodium hydride furnished the salt **13**. **13** underwent thermal decomposition to form the diazo compound **14** at an unusually low temperature (50 °C). As in the case of the ketones **10** and **10′**, the ^{1}H NMR spectrum of **14** indicates the presence of a small amount of the Z isomer (see Experimental Section). Flash vacuum pyrolysis of **14** at 400 °C gave the known[6] spiro compound **16**. At 600 °C, flash pyrolysis of either **14** or **16** yielded 1*H*-cyclopent[*cd*]indene (**18**), which has also been prepared by other routes.[7] The results indicate that **16** reopens to the benzofulvenylcarbenes **15** and **17** at ca. 600 °C, the latter cyclizing to **18**.

Scheme III



At a still higher temperature, 800 °C, a 1,2-hydrogen shift in the carbenes **15** $\rightleftharpoons$ **17** took place, to give 1-vinylideneindene (**19**) together with **18** (ratio of **19:18** ca. 1:2). Thus, the formation of **18** and **19** is considered to be the result of competing reactions of the carbenes. While **18** can be freed from **19** by vacuum distillation at 0–25 °C, **19** has not been isolated in pure form due to partial polymerization at room temperature. Yet, **19** is far more stable than its blue isomer, 2-vinylidene-2*H*-indene, whose identification was achieved recently by infrared and photoelectron spectroscopy.[8] The allene **19** was identified primarily by condensing the pyrolysate directly on a turnable KBr disk at −196 °C, whereby a strong IR absorption at 1935 cm^{-1} (>C=C=CH$_2$) was observable; in the ^{1}H NMR spectrum this function appeared at δ 5.4, close to the position of the corresponding peak in the parent compound, viz. 1-vinylidenecyclopentadiene (fulveneallene) (**25**). Furthermore, **19** was also obtained, albeit in low yield, by ring contraction of 1-naphthylcarbene at 800 °C,[9] a reaction analogous to the transformation of phenylcarbene (**20**) to fulveneallene (**25**)[10] (Scheme III).

The formation of allene **19** from the fulvenylcarbenes (**15** $\rightleftharpoons$ **17**) is highly significant in relation to the mechanism of ring contraction in phenylcarbene[10,11] (Scheme III). On the basis of labeling experiments, the path via **21** and **22** was indicated. Ring opening in **22** leads to the diradical **23** and/or the fulvenylcarbene **24**.[12] Since **24** was otherwise unknown, independent evidence that such a carbene would undergo a 1,2-hydrogen shift to give an allene (**25**) was desirable. This has been provided by the present work.

Experimental Section

General Procedures. Pyrolyses were carried out in apparatus A previously described[1] at 10^{-3} to 10^{-4} torr. The products were collected on a cold finger cooled with liquid N_2. ^{1}H NMR spectra were recorded on Varian T60 or XL-100, mass spectra on Varian CH-7 (70-eV electron impact) or MAT-711 (field desorption), and IR spectra on Beckmann IR 18A instruments. Microanalyses were performed by Mr. Pfeiffer in the microanalytical laboratory of this department.

2-Phenyl-5-(2-furyl)tetrazole (4) was prepared in 42% yield according to Ito et al.[2] The 70-eV electron-impact mass spectrum showed no molecular ion, but gave m/e 184 ($M^+ - N_2$, 20%) and 91 (C_6H_5N, 100), which are characteristic of 2-phenyl-5-aryltetrazoles.[1] The molecular ion (m/e 212, 100%) was obtained by field desorption ionization. The NMR spectrum is described

(5) M. N. Nwaji and O. S. Onyiriuka, *Tetrahedron Lett.*, 2255 (1974).
(6) T. Severin, H. Krämer, and P. Adhikary, *Chem. Ber.*, **104**, 972 (1971).
(7) P. Eilbracht and K. Hafner, *Angew. Chem.*, **83**, 802 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 751 (1971); B. L. McDowell and H. Rapoport, *J. Org. Chem.*, **37**, 3261 (1972).
(8) C. Wentrup, E. Wentrup-Byrne, P. Müller, and J. Becker, *Tetrahedron Lett.*, 4249 (1979); R. Schulz, A. Schweig, C. Wentrup, and H.-W. Winter, to be published.
(9) J. Becker and C. Wentrup, to be published; the major thermal reaction product of 1-naphthylcarbene is cyclobuta[*de*]naphthalene (J. Becker and C. Wentrup, *Chem. Commun.*, in press).
(10) C. Wentrup, E. Wentrup-Byrne, and P. Müller, *Chem. Commun.*, 210 (1977).
(11) C. Wentrup, *Chimia*, **31**, 258 (1977); C. Wentrup in "Reactive Intermediates", Vol. 1, R. A. Abramovitch, Ed., Plenum Press, London, New York, in press.
(12) In the absence of a detailed knowledge of the electronic structure of **23** and **24**, we cannot say whether these are different species or different canonical forms of the same species.

in Table I; IR (KBr) 3060 (w), 1625 (s), 1600 (s), 1500 (s), 1480 (m), 1450 (s), 1230 (s), 1190 (m), 1070 (m), 1000 (s), 900 (s), 760 (s) cm^{-1}.

3-(2-Furyl)indazole (7). 4 (370 mg, 1.75 mmol) was pyrolyzed at 400 °C by slow sublimation from a sample flask held at 61 °C (10^{-4} torr). A volatile product condensed on the cold finger. A less volatile product condensed in the uncooled zone between the oven and the cold finger. The less volatile product was recrystallized from CCl_4 to give 128 mg (40%) of 7: colorless needles, mp 165–166 °C; NMR, see Table I; IR (KBr) 3200–2800 (br), 1610 (m), 1450 (m), 1325 (s), 1230 (s), 1000 (s), 980 (s), 880 (s), 760 (s), 715 (s) cm^{-1}; mass spectrum, m/e 184 (M^+, 100), 155 (36), 91 (11), 77 (7). Anal. Calcd for $C_{11}H_8N_2$: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.65; H, 4.26; N, 15.20.

The more volatile product (18%) was identified as **10** as below.

Benzofulvene-8-carboxaldehyde (10). A pyrolysis of 1.0 g (4.7 mmol) of 4 at 720 °C (10^{-3} torr) gave a yellow product on the cold finger. This was freed from polymer (150 mg) by filtering a CH_2Cl_2 solution through Al_2O_3 (activity grade III). Subsequent removal of the solvent and sublimation at 85 °C (0.05 torr) furnished 470 mg (64%) of **10**: mp 88 °C (lit.[4] 90 °C); NMR ($CDCl_3$) δ 6.76 (dd, J = 8 and 1 Hz, 1 H), 7.03–7.76 (m, 6 H), 10.40 (d, J = 8 Hz, 1 H; CHO)[4] (this spectrum is ascribed to the E isomer (**10**); small doublets at δ 6.33 and 10.83 ($J \simeq 8$ Hz) may be due to the Z isomer (**10′**) (E/Z = 9:1)); IR (KBr) 3040 (w), 1660 (s), 1600 (w), 1450 (m), 1120 (m), 870 (m), 800 (m), 750 (s), 720 (m) cm^{-1}; mass spectrum, m/e 156 (M^+, 98), 155 (27), 128 (100), 127 (38).

Benzofulvene-8-carboxaldehyde Tosylhydrazone (12). A solution of 800 mg (5.12 mmol) of **10** and 960 mg (5.16 mmol) of tosylhydrazine in absolute methanol was stirred for 8 h; on concentration in vacuo, 998 mg (60%) of the tosylhydrazone (**12**) crystallized: mp 125 °C; NMR ($CDCl_3$) δ 2.40 (s, 3 H), 6.66 (d, J = 5 Hz, 1 H), 6.84–8.11 (complex, 11 H), 8.90 (br, 1 H, NH); IR (KBr) 3200 (m), 1590 (m), 1445 (s), 1355 (s), 1315 (s), 1160 (s), 1050 (s), 895 (s), 810 (s), 745 (s), 720 (m), 655 (s) cm^{-1}; mass spectrum (field desorption), m/e 324 (M^+, 100), 169 (26), 139 (93).

1-(2-Diazoethylidene)indene (14). Absolute methanol was added dropwise to a suspension of **12** (0.6 g, 1.8 mmol) in 70 mL of absolute ether until dissolution was complete. A suspension of sodium hydride (44 mg, 1.8 mmol) in ether was then added slowly to the magnetically stirred solution, which was kept under N_2 and in the dark. Rapid H_2 evolution took place and the tosylhydrazone sodium salt (**13**) precipitated after a few minutes. After the solution was stirred for 2 h, the salt was filtered under N_2, washed with ether, and dried under high vacuum in the dark. The yield was 620 mg. This salt was not examined further, but heated at 50–60 °C (10^{-3}–10^{-4} torr) in a flask attached to a cold trap cooled in liquid N_2. The orange-red solid which condensed in the trap was identified as 1-(2-diazoethylidene)indene (**14**) by comparison with a sample prepared by the method of Severin:[6] IR (CCl_4) 3030 (w), 2940 (w), 2050 (vs), 1585 (s); IR (KBr) 2050 (vs), 1570 (s), 1420 (m), 1380 (s), 1285 (m), 1240 (s), 975 (m), 765 (m), 735 (s), 700 (s) cm^{-1}; NMR (CCl_4) δ 5.3 (d, J = 10 Hz, 1 H, CH=N_2), 6.5 (d, $J \simeq 5$ Hz, 1 H, H-3), 6.75 (d, $J \simeq 5$ Hz, 1 H, H-2), 6.85 (d, J = 10 Hz, 1 H, H-8), 7.0–7.4 (m, 4 H); this spectrum is ascribed to the E isomer (**14**). A small doublet at δ 5.67 ($J \simeq$ 10 Hz) may be due to the CH=N_2 group of the Z isomer ($E/Z \simeq$ 8:1).

Pyrolysis of 1-(2-diazoethylidene)indene was carried out either by decomposition of the tosylhydrazone salt **13** at 50–60 °C or by sublimation of the pure diazo compound **14** at 20–50 °C unless otherwise indicated. The vapors were led directly into the pyrolysis tube at the desired temperature. In both cases, the yields of the pyrolysis products described below were generally poor (15–20%) due to partial decomposition of **14** in the sublimation flask with the formation of a crust, which prevented the major part of **14** from volatilizing.

(a) At 300 °C the pyrolysate was orange and shown by NMR to consist of unchanged **14**.

(b) At 400 °C a colorless pyrolysis product formed on the cold finger. This was vacuum transferred at room temperature and identified as spiro[cyclopropene-1,1′-indene] (**16**) by comparison of the NMR spectrum with that of an authentic sample.[6]

(c) At 600 °C a white crystalline material formed, mp ~0 °C, which was vacuum transferred at 0–25 °C (10^{-2} torr): NMR (CCl_4) δ 3.97 (d, $J \simeq$ 1.5 Hz, 2 H), 6.62 (m (three peaks), 2 H), 7.16 (narrow m, 4 H), identical with the spectra previously reported[7] for 1*H*-cyclopent[*cd*]indene (**18**).

(d) When the 600 °C pyrolysis was carried out by using very rapid sample introduction (decomposition of **13** at 90–100 °C), **18** was still the main product as shown by NMR, but the orange color and a weak absorption at 2050 cm^{-1} in the IR indicated that a trace of the diazo compound (**14**) survived even this temperature, thereby testifying to the mildness of the procedure.

(e) At 800 °C the pyrolysate was yellow: IR (KBr, −196 °C) 1935 (vs) cm^{-1} (C=C=CH_2); NMR ($CDCl_3$) as reported under c for **18**, together with a new peak at δ 5.43 (C=C=CH_2) due to **19**.[9] The ratio **18**:**19** ~ 2:1 was determined by integration. **18** could be removed from **19** by distillation at 0–25 °C (0.1–0.001 torr); only very little of the allene distilled under these conditions as shown by NMR and IR analyses. The distillation residue was a yellow-brown oil which, according to the IR spectrum, contained no allene function.

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Registry No. 4, 60637-07-2; 7, 3878-19-1; 10, 73017-90-0; 10′, 73017-91-1; 12, 73017-92-2; 13, 73017-93-3; (*E*)-14, 73017-94-4; (*Z*)-14, 73017-95-5; 16, 31337-05-0; 18, 209-69-8; 19, 73017-96-6.

Reactions of 1,1-Diarylethylenes and 1,1-Diarylimines with CF_3OF

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1,1-Diphenylethylene (**1**) reacts with CF_3OF to give products **2**–**6** in a cationic process. 9-Ethylidenefluorene reacts with CF_3OF to yield **8** and **10**. Amitriptyline (**12**) furnished a difluoro adduct (**13**) in low yield. Benzophenone oxime (**14**) gave a Beckmann rearrangement product on reaction with CF_3OF. Fluorenone anil (**15**) produced mainly fluorenone from reaction with CF_3OF. Diazepam (**16**) gave a 1:1 adduct (**18**) with CF_3OF. The adduct **18** reacted further to give an oxidation product (**17**).

Diarylethylenes have received considerable attention in synthetic and mechanistic organofluorine chemistry. 1,1-Diphenylethylene (**1**) has been subjected to fluorination under a variety of conditions and has provided some in-

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