Molecules **2000**, *5*, 1004-1010

molecules

ISSN 1420-3049

http://www.mdpi.org

Flash Vacuum Pyrolysis of 2,5-Diphenyloxazole

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Received: 28 January 2000; revised form 21 July 2000 / Accepted: 1 August 2000 / Published: 9 August 2000

Abstract: FVP of the title oxazole (**1**) at 1000°C and 0.5 mm Hg afforded a complex reaction mixture containing benzonitrile, phenylacetonitrile, biphenyl, diphenylmethane, fluorene, *o*-benzylbenzonitrile (major product, 22%), phenanthrene, anthracene, 9,10-anthraquinone, 2-phenylindole and 3-phenylindole. A radical and carbene mechanism was suggested in order to rationalize the formation of the reaction products.

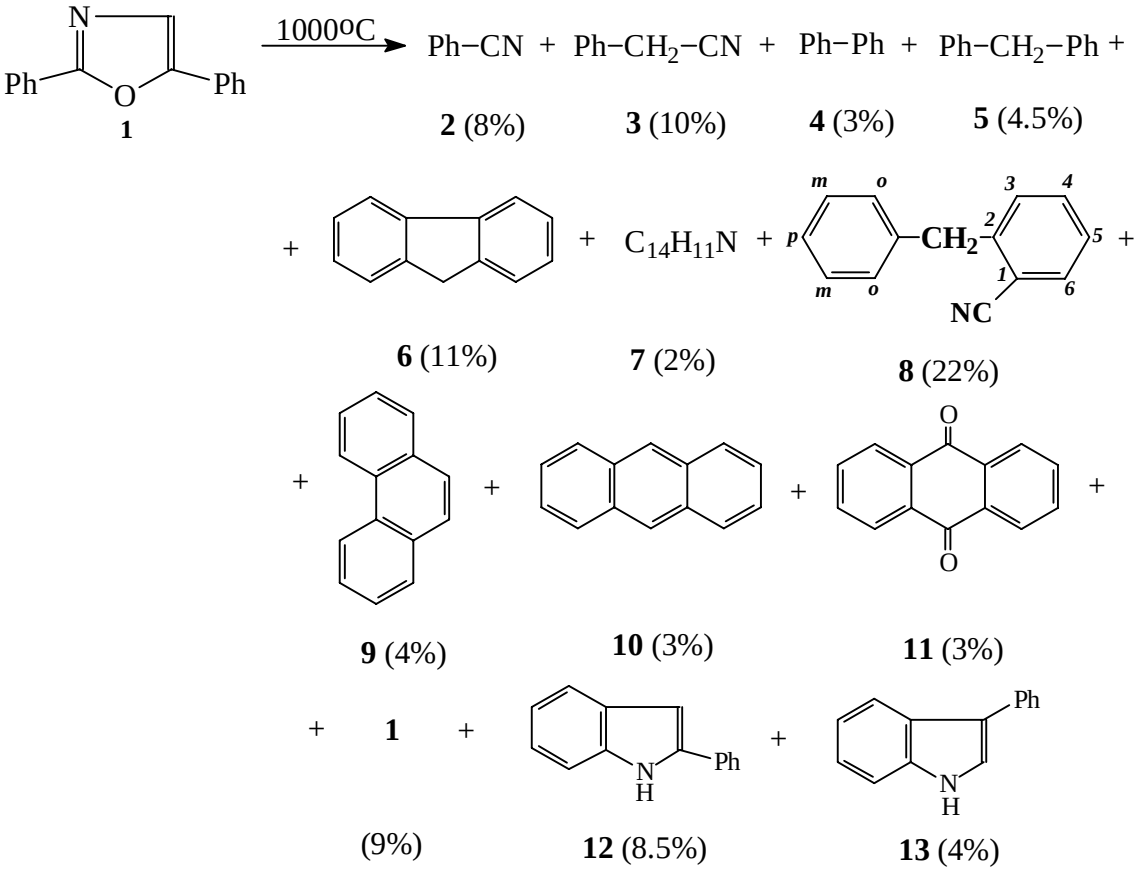
Keywords: Flash-vacuum pyrolysis, 2,5-diphenyloxazole, radical reactions, carbenes.

Introduction

The thermal behaviour of a large variety of heterocyclic compounds has been investigated in connection with mechanistic and/or synthetic studies [1-3]. Though flash-vacuum pyrolyses (FVP) of a few substituted and annulated isoxazoles [4-6] as well as of different isoxazolones [7-9] were investigated (revealing the preferential fission of the N-O bond, and the extrusion of CO_2, respectively) reports on the gas-phase chemistry of oxazoles are very scarce. Thus, it has been proved that unsubstituted oxazole radical cation dissociates by elimination of a hydrogen atom [10] whereas 2-phenyl-1,3-oxazol-5(4H)-one thermally eliminates CO_2 [11]. In order to provide supplementary data concerning FVP of oxazoles and in continuation of our previous investigations of FVP of hydrocarbons [12] and heterocycles [13], we intend to study the thermal behaviour of a series of substituted oxazoles. In the present paper we describe the results of FVP of 2,5-diphenyloxazole (**1**).

Results and Discussion

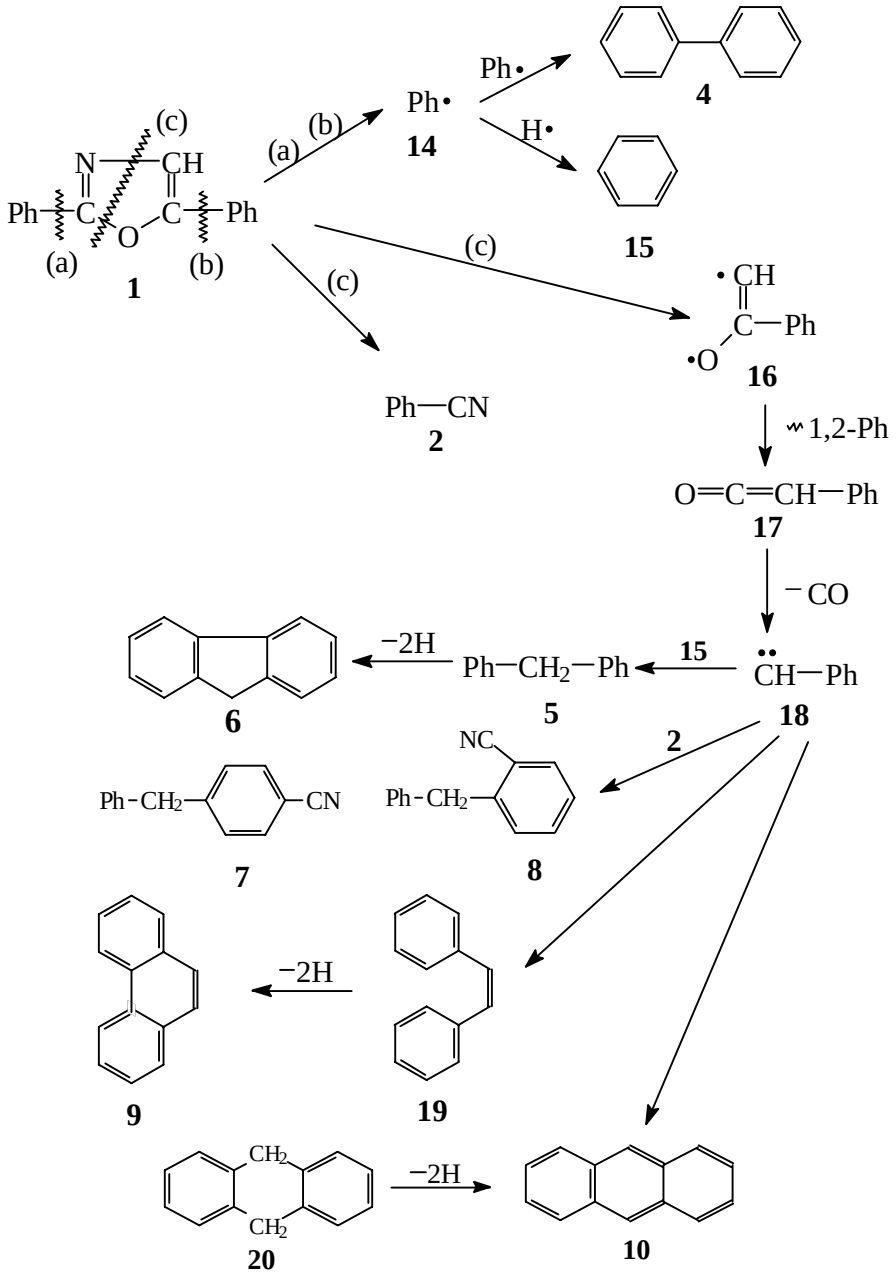
The pyrolyses of diphenyloxazole **1** were performed in a flow-system under argon atmosphere at 0.5 mm Hg, the calculated contact times being ≤ 0.2 s. Under these conditions the oxazole **1** showed a high thermal stability. Whereas at 800°C a conversion of only 9% was achieved, the increase of temperature at 1000°C brought the conversion to 91%. The reaction products were examined by GC/MS analysis and by ^{1}H- and ^{13}C-NMR spectroscopy. The product distribution was a very complex one. The pyrolysis products are shown in Scheme 1 in the order of their elution from the GC column.



Scheme 1.

From the reaction products compounds **2-6** and **9-13** were identified by their characteristic mass spectra which were favourably compared with the mass spectra of authentic specimens. For compounds **2**, **3**, **4**, **6**, **9**, **10** and **11** mixed GC analysis of mixtures of the pyrolysis product with authentic samples also confirmed the proposed structures. Compound **8**, the main pyrolysis product, was separated by column chromatography on silica and identified through its spectral data (see also Experimental) as follows: the infrared spectrum indicated the characteristic absorption of a CN group (2231 cm^{-1}) along with those of CH_2 groups and aromatic moieties. In the ^{1}H-NMR spectrum a singlet at δ = 4.21 ppm can be attributed to the CH_2 protons (the deshielding of 0.25 ppm as compared to diphenylmethane being due to the *ortho*–CN group). Doping the sample of **8** with Eu(fod)$_3$ shift reagent led to a larger molar induced shift (1.9) for H^6 than for H^3 – H^5. A molar induced shift of 1.4 was observed for CH_2 protons situated in the vicinity of the CN complexing group. The ^{13}C-NMR spectrum of **8** indicated the signal of CH_2 at δ = 40.21 ppm and that of CN at δ = 118.11 ppm. The ^{13}C chemical shifts of all carbon

atoms calculated using known increments agree well with the experimental values. Compound **7**, occuring in a small amount (2%), seems to be a steric isomer of **8**, giving M=193 and a molecular formula of $C_{14}H_{11}N$ (probably possessing the -CN group in the *para* position). The increased thermal stability of diphenyloxazole **1** is due to the lack of easily eliminable moieties (like e.g. N_2 or CO_2 in other heterocycles) as well as in the absence of bonds particularly prone to cleavage (like the N-O bond in isoxazoles). The two phenyl substituents conjugated with the oxazole ring also contribute to the stability of **1**.



Scheme 2.

In order to rationalize the formation of the main pyrolysis products a reaction scheme including more competing pathways can be proposed (Scheme 2). Compounds **2**, **4-10** can be generated from **1** by bond cleavage routes denoted (a), (b), (c) in Scheme 2. Generation of free radicals seems to be favoured by the reaction conditions (1000°C; quartz apparatus). Phenyl radicals can generate biphenyl (**4**) and

benzene (identified in traces), whereas fission (c) affords benzonitrile (**2**). On the other hand, in the diradical **16** an usual 1,2-phenyl migration could lead to the intermediate occurrence of phenylketene **17**. Thermal decarbonylations of ketenes to carbenes are well-known processes [14]. The phenylcarbene **18**, generated from **17** can be the precursor of **5** and **6** (by insertion and hydrogen elimination), of **7** and **8** (by insertion) and of **9** and **10** (by dimerisation respectively double insertion followed by dehydrogenation). Previous work by Hedaya [15] has shown that the reaction products of phenylcarbene - generated from phenyldiazomethane - are strongly determined by the reaction conditions employed, especially by the temperature (the increase of anthracene at 900°C being underlined).

Conclusions

The high thermal stability and the narrow temperature interval of pyrolysis of 2,5-diphenyloxazole were demonstrated. Among the twelve identified pyrolysis products, the most abundant (22%) is *o*-benzylbenzonitrile. The suggested reaction mechanism will be further tested and/or detailed by investigation of other substituted oxazoles.

Experimental

General

Melting points are uncorrected. The NMR spectra were registered on a Varian Gemini 300 apparatus at 300 MHz for ^{1}H and at 75 MHz for ^{13}C, using TMS as internal standard. The GC/MS analyses were performed on a Varian 3400 gas chromatograph with split/splitless injector coupled with a Varian Saturn II mass spectrometer provided with ion trap. A capillary DB-5 column (30m length, 0.25 mm internal diameter) was used. The analysis conditions were: injector temperature 250°C, split rate 1:50, temperature program 50-250°C at 7°/min, then 20 min. at 250°C, carrier gas helium with flow-rate 1 mL/min., temperature of transfer line 200°C, trap temperature 170°C, electron ionization 70 eV.

2,5-Diphenyloxazole (**1**)

M.p. 71-72°C, was a commercially available product (Aldrich).

FVP of 2,5-Diphenyloxazole

All FVP were performed in a flow system using a previously described apparatus [16]. The pyrolysis quartz tube (60 cm length, 10 mm diameter) was filled with quartz chips on 30 cm length; this zone was heated with a cylindrical electric oven. The temperature was continously measured by means of a thermocouple and the pressure (0.5mm Hg) with a McLeod manometer. The oxazole sample (usually 30 mg) was sublimed under argon flow (4 mL/min.) in the pyrolysis zone. The reaction products accumulated at the cooled end of the quartz tube were dissolved in chloroform, the solvent was evaporated *in vacuo* and the residue (about 85% yield) was subjected to GC/MS analysis. Pyrolysis of **1** at 800°C conducted to only 9% conversion. Working at 1000°C a conversion of 91% was achieved. The reaction products in this case were, in order of their elution from GC column: benzene (**15**) (only traces due to its high volatility); benzonitrile (**2**) - 8%; phenylacetonitrile (**3**) - 10%; biphenyl (**4**) - 3%; diphenyl-

methane (**5**) - 4.5%; fluorene (**6**) - 11%; unknown component with M=193 (**7**) - 2% (probably the *para* isomer of **8**); *o*-benzylbenzonitrile (**8**) - 22%; phenanthrene (**9**) - 4%; anthracene (**10**) - 3%, 9,10-anthraquinone (**11**) - 3%; unreacted oxazole **1** - 9%; 2-phenylindole (**12**) - 8.5% and 3-phenyl-indole (**13**) - 4%. Along with these products, representing 92% from the reaction mixture, only minor components (< 2%) were observed in the gas-chromatogram. These minor components were not further investigated. From the above reaction products the compounds **2**-**6** and **9**-**13** were identified by their characteristic mass spectra which were favourably compared with the mass spectra of authentic specimens registered in the GC/MS library. For some reaction products (**2**, **3**, **4**, **6**, **9**, **10** and **11**) mixed GC samples of pyrolysis product with authentic specimens confirmed the proposed structures. The mass spectra of components **5**, **7**, **8**, **12** and **13** are given below:

*Diphenylmethane (***5***)*

Mass spectrum (m/z; relative abundance %): 27 (3); 38 (3); 39 (15); 50 (6); 51 (9); 62 (2); 63 (8); 65 (11); 76 (2); 77 (3); 83 (2); 89 (9); 90 (3); 91 (40); 92 (3); 102 (2); 113 (2); 115 (10); 126 (2); 128 (4); 139 (5); 141 (3); 151 (2); 152 (25); 153 (30); 154 (4); 163 (3); 164 (4); 165 (37); 166 (11); 167 (100; P.I.; M); 168 (87; M+1); 169 (10; M+2).

*Benzylbenzonitrile (***7***)*

Mass spectrum (m/z; relative abundance %): 26 (6); 27 (9); 28 (59); 38 (8); 39 (21); 50 (26); 51 (43); 52 (7); 62 (10); 63 (21); 74 (9); 75 (8); 76 (16); 77 (19); 87 (5); 88 (7); 89 (32); 90 (9); 102 (6); 115 (12); 116 (14); 139 (6); 151 (6); 152 (12); 163 (5); 164 (6); 165 (90); 166 (35); 167 (7); 176 (6); 177 (6); 178 (37); 179 (50); 180 (43); 181 (7); 190 (6); 191 (6); 192 (24); 193 (100; P.I.; M); 194 (21; M+1); 195 (0.5; M+2).

*o-Benzylbenzonitrile (***8***)*

Mass spectrum (m/z; relative abundance %): 27 (3); 37 (2); 38 (3); 39 (11); 50 (6); 51 (8); 52 (2); 62 (3); 63 (8); 64 (2); 65 (7); 74 (2); 75 (3); 76 (3); 77 (3); 87 (2); 88 (2); 89 (9); 90 (4); 91 (7); 113 (2); 115 (3); 116 (4); 118 (2); 139 (3); 140 (3); 145 (3); 151 (2); 152 (4); 163 (5); 164 (5); 165 (43); 166 (8); 177 (3); 178 (4); 179 (4); 180 (6); 190 (8); 191 (5); 192 (27); 193 (100; P.I.; M); 194 (21; M+1); 195 (2; M+2).

*2-Phenylindole (***12***)*

Mass spectrum (m/z; relative abundance %):. 27 (2); 38 (2); 39 (5); 50 (3); 51 (3); 62 (2); 63 (3); 74 (2); 82 (2); 83 (2); 87 (2); 89 (3); 90 (2);115 (2); 139 (3); 163 (5); 164 (6); 165 (27); 166 (5); 167 (2); 190 (2); 191 (4); 192 (15); 193 (100; P.I.; M); 194 (16; M+1); 195 (1; M+2).

*3-Phenylindole (***13***)*

Mass spectrum (m/z; relative abundance %):. 39 (4); 50 (2); 51 (2); 63 (3); 89 (7); 90 (3); 139 (2); 163 (2); 164 (2); 165 (17); 166 (3); 167 (2); 190 (2); 191 (4); 192 (14); 193 (100; P.I.; M); 194 (16;

M+1); 195 (1; M+2).

For preparative purposes the products of four identical pyrolyses at 1000°C were combined and subjected to liquid chromatography on a silica column (Merck 60; 35-70 mesh) using petroleum ether: diethylether (95:5) as eluent. The separated *o*-benzylbenzonitrile (thick oil; lit. m.p. [17] = 19°C) gave the following spectral data:

IR Spectrum (CCl_4; cm^{-1}): 1458 (δ_{CH_2}); 2231 (ν_{CN}); 2853 ($\delta_{CH_2}^{sim}$); 2961 ($\delta_{CH_2}^{asim}$); 3025 and 3061 (δ_{CH}).

^{1}H-NMR Spectrum ($CDCl_3$, δ ppm, *J* Hz;): 4.21 (s;2H; CH_2); 7.20-7.35 (m; 7H; C_6H_5; H^5; H^3); 7.49 (td; 1H; 7.7; 1.5; H^4); 7.63 (dd; 1H; 1.4; H^6).

^{13}C-NMR Spectrum ($CDCl_3$, δ ppm,): 40.21 (CH_2); 112.67 (C^1); 118.11 (CN); 126.71 (CH^{para}); 126.77 (C^5); 128.72 (2 CH^{meta}); 128.98 (2 CH^{ortho}); 130.05 (C^3); 132.83 (C^6); 132.90 (C^4); 138.79 (C_{quart}); 144.98 (C^2).

Acknowledgements: The authors express their thanks to Professor Iosif Schiketanz for a sample of 2,5-diphenyloxazole and to Professor Alexandru T.Balaban for helpful discussions.

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Sample Availability: Available from the authors.