1,3-Dipolar Cycloaddition Reactions of Benzonitrilium *N*-Phenylimide with 3-Arylmethylene-5-phenylfuran-2(3*H*)-ones†

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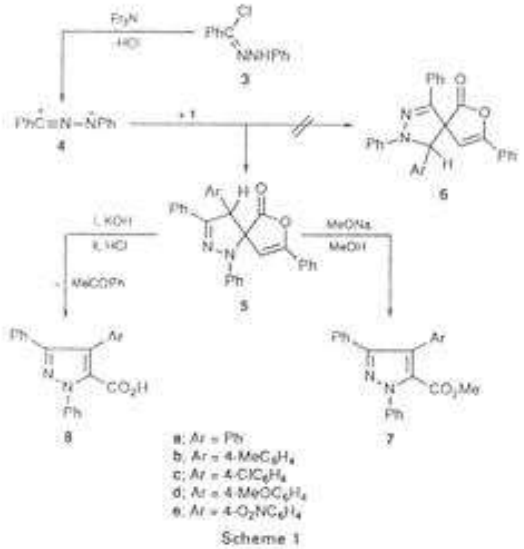
4-Aryl-1,3,8-triphenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-dien-6-ones have been prepared by the reaction of *N*-phenyl benzohydrazonoyl chloride with 3-arylmethylene-5-phenylfuran-2(3*H*)-ones in chloroform in the presence of triethylamine.

Although (*E*)-3-arylmethylene-5-phenylfuran-2(3*H*)-ones (**1**) are isoelectronic with (*Z*)-4-arylmethylene-2-phenyloxazol-5(4*H*)-ones (**2**), the 1,3-dipolar cycloaddition reactions of **1** have not yet been explored as is the case with **2**.[1–4] In this paper the reactions of phenylacetonitrilium *N*-phenylimide (**4**) with **1a–e** are studied and the regiochemistry of the cycloadducts is determined (Scheme 1).

1 **2**

The nitrile imide **4**, generated *in situ* by the action of triethylamine on *N*-phenylbenzohydrazonoyl chloride (**3**) in benzene at reflux, reacted with **1a–e** to give the corresponding cycloadducts **5a–e** in good yields (74–82%). As in the case of the reactions of **2** with **4**, the reactions in this study are regioselective and in each case only one regioisomer of **5** was isolated. This regioselectivity was evidenced from ^{1}H NMR analysis of the crude reaction product.

The structural assignment of the isolated spiropyrazoles **5** was made on the basis of their chemical transformations (Scheme 1) and spectral data (^{1}H and ^{13}C NMR). Thus, when the cycloadduct obtained from the reaction of **1a** with **4**, taken as a typical example of the series studied, was refluxed in methanol in the presence of sodium methoxide it gave methyl 1,3,4-triphenylpyrazole-5-carboxylate (**7a**). In addition, hydrolysis of the same cycloadduct by heating with potassium hydroxide in aqueous ethanol at reflux temperature yielded acetophenone and the pyrazolecarboxylic acid **8a**. Treatment of the latter acid with diazomethane in diethyl ether afforded **7a**. Both the ester **7a** and the acid **8a** were prepared independently according to known procedures.[5,6] The by-product acetophenone was identified by its conversion into its *p*-nitrophenylhydrazone derivative.[7] These results indicate that the cycloadducts isolated have structure **5** and not the regioisomeric structure **6**.



a; Ar = Ph
b; Ar = 4-MeC_6H_4
c; Ar = 4-ClC_6H_4
d; Ar = 4-$MeOC_6H_4$
e; Ar = 4-$O_2NC_6H_4$

Scheme 1

This conclusion was further supported by comparison of the chemical shift of the 4-CH proton of the pyrazole ring residue of **5a–e** with those of the related compounds **11**[1] and **12**.[2] Thus, the ^{1}H NMR spectra of **5a–e** in [^{2}H]chloroform showed in each case two singlets in the regions δ 5.05–5.15 and 5.30–5.45. These were assigned to the 4-CH and 3-CH protons of the pyrazole and furanone ring residues respectively. Such assignments were confirmed by the ^{13}C NMR spectral data. For example, the ^{13}C NMR spectrum of **5b** revealed the signals for the carbon atoms of these groups as two doublets centred at δ 63.0 and 102.5 respectively, whereas that of the spiro-carbon atom was seen as a singlet at δ 78.4. The ^{13}C NMR of **1b** showed the 3-CH signal as a doublet at δ 100.0. The similarity between the proton chemical shifts for the 4-CH group of **5a–e** and those reported for compounds **11** (δ 5.20–5.30) and **12** (δ 5.32–5.70)[1,2] supports the assigned structure **5**. The chemical shift of such a proton would be shifted downfield had the addition of **4** to **1** taken place in the opposite direction to give **6**. Recently, it has been shown that the chemical shift of the 5-CH proton is larger than that of the 4-CH proton of 4,5-dihydro-1*H*-pyrazole derivatives.[7]

11 **12**

Experimental

Reactions of **4** *with* **1a–e**. *General Procedure*.—To a solution of the appropriate furanone **1**[8] (10 mmol) and *N*-phenylbenzohydrazonoyl chloride **3**[9] (2.3 g, 10 mmol) in dry benzene (40 ml) was added triethylamine (1.4 ml, 10 mmol) and the mixture was refluxed for 2 h, then cooled. The solid which precipitated was filtered off, washed with aqueous ethanol and finally crystallized from dimethylformamide to give the corresponding *4-aryl-1,3,8-triphenyl-7-oxa-1,2-diazaspiro[4.4]nona-2,8-dien-6-one* **5**: **5a** (82%, yield), m.p. 230 °C, ν_{max}/cm^{-1} (KBr) 1802 (C=O); δ ($CDCl_3$) 5.06 (1 H, s), 5.30 (1 H, s), 6.9–7.8 (20 H, m) (Found: C, 80.9; H, 5.0; N, 6.4. $C_{31}H_{24}N_2O_2$ requires C, 81.42; H, 5.01; N, 6.13%). **5b** (80% yield), m.p. 219 °C, ν_{max}/cm^{-1} (KBr) 1802 (C=O); δ ($CDCl_3$) 2.35 (3 H, s), 5.05 (1 H, s), 5.42 (1 H, s), 7.0–7.8 (19 H, m) (Found: C, 81.4; H, 5.4; N, 6.1. $C_{32}H_{26}N_2O_2$ requires C, 81.55; H, 5.30; N, 6.14%). **5c** (76% yield), m.p. 181 °C, ν_{max}/cm^{-1} (KBr) 1803 (C=O); δ ($CDCl_3$) 5.06 (1 H, s), 5.35 (1 H, s), 7.0–8.0 (19 H, m) (Found: C, 75.3; H, 4.4; N, 5.7. $C_{31}H_{23}ClN_2O_2$ requires C, 75.50; H, 4.44; N, 5.87%). **5d** (78% yield), m.p. 178 °C, ν_{max}/cm^{-1} (KBr) 1802

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(C=O); δ($CDCl_3$) 3.75 (3 H, s), 5.05 (1 H, s), 5.32 (1 H, s), 6.7–7.8 (19 H, m) (Found: C, 78.6; H, 5.0; N, 5.9. $C_{31}H_{24}N_2O_3$ requires C, 78.79; H, 5.12; N, 5.93%). **5e** (71% yield), m.p. 216 °C; ν_{max}/cm^{-1} (KBr) 1805 (C=O); δ($CDCl_3$) 5.15 (1 H, s), 5.30 (1 H, s), 7.0–8.3 (19 H, m) (Found: C, 73.8; H, 4.4; N, 8.5. $C_{30}H_{21}N_3O_4$ requires C, 73.91; H, 4.34; N, 8.62%).

Methanolysis of **5a**.—A solution of **5a** (1.63 g, 3 mmol) and sodium methoxide (3 mmol) in methanol (25 ml) was refluxed for 6 h and cooled. The resulting solution was neutralized with hydrochloric acid (20%). The solid which precipitated upon neutralization was filtered off, washed with water and dried. The crude product was purified by column chromatography using silica gel as adsorbent and hexane–ethyl acetate (10:1 v/v) as eluent to give the ester **7a**, m.p. 129 °C (lit.,[3] 129 °C), identical (IR, NMR) with an authentic sample.[3]

Hydrolysis of **5a**.—To a solution of **5a** (1.63 g, 3 mmol) in ethanol (40 ml) was added aqueous potassium hydroxide (10 ml, 6 M) and the mixture was refluxed for 6 h, then cooled. The reaction mixture was acidified with hydrochloric acid (30%). The crude solid which precipitated upon acidification was collected, washed with water and crystallized from methanol to give the acid **8a** in 94% yield, m.p. 224–225° (decomp.) (lit.,[4] 225 °C), identical (IR, NMR) with an authentic sample.[3] Treatment of **8a** with diazomethane in dry diethyl ether afforded **7a**, identical with the sample above.

Addition of ethanolic solution of *p*-nitrophenylhydrazine to the filtrate remaining after removal of the crude acid **8** and warming of the mixture precipitated an orange-red solid. Recrystallization from ethanol gave acetophenone *p*-nitrophenylhydrazone, m.p. 185 °C (lit.,[5] 184–185 °C).

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