Synthetic Approaches towards New Bisformazans and Bisverdazyls

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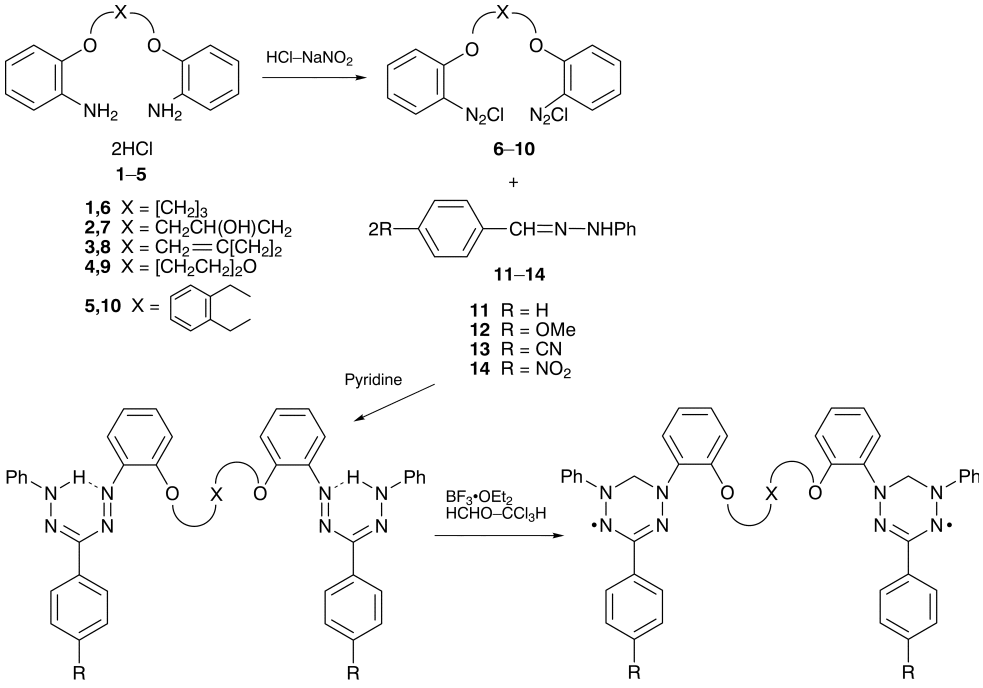
The new bisformazans **15**–**23**, **28** and **29** are prepared *via* three routes and some are converted into the corresponding bisverdazyls **34**–**37** which represents a new class of stable diradicals.

Much attention has been directed towards the chemistry of formazans owing to their diverse applications in many fields.[1,5,8,27] Moreover, verdazyls discovered by Kuhn and Trischman[17,18] represent a class of extraordinary stable free radicals with many interesting applications.[26] The present investigation describes three synthetic routes for the synthesis of the bisformazans **15**–**23**, **28** and **29** (Schemes 1 and 2) and the conversion of some to the corresponding bisverdazyls **34**–**37**.

Thus, coupling of the bisdiazonium salts **6**–**10** (prepared from the corresponding bisamines **1**–**5**) with the appropriate araldehyde phenylhydrazones **11**–**14** in pyridine gave the corresponding bisformazans **15**–**23** in 56–64% yield. Following a recent recommended method using phase transfer catalytic synthesis of formazans[29] the yields of compounds **17**, **19** and **21** were increased to 69–70% when the coupling reaction was carried out in dichloromethane containing either Na_2CO_3 or NaOH and tetrabutylammonium iodide as PTC.

On the other hand, the bisformazans **28** and **29** were prepared from the biscarboxaldehyde derivatives **30**, **31** by converting them into the corresponding bisphenylhydrazones followed by coupling with benzenediazonium chloride in pyridine. Alternatively, compound **28** was prepared



Compound	X	R
15	$[CH_2]_3$	H
16	$[CH_2]_3$	OMe
17	$[CH_2]_3$	CN
18	$[CH_2]_3$	NO_2
19	$CH_2CH(OH)CH_2$	H
20	$CH_2{=}C[CH_2]_2$	H
21	$[CH_2CH_2]_2O$	CN
22		H
23		OMe

Compound	X	R
34	$[CH_2]_3$	H
35	$[CH_2]_3$	OMe
36	$[CH_2]_3$	CN
37	$[CH_2CH_2]_2O$	CN

Scheme 1

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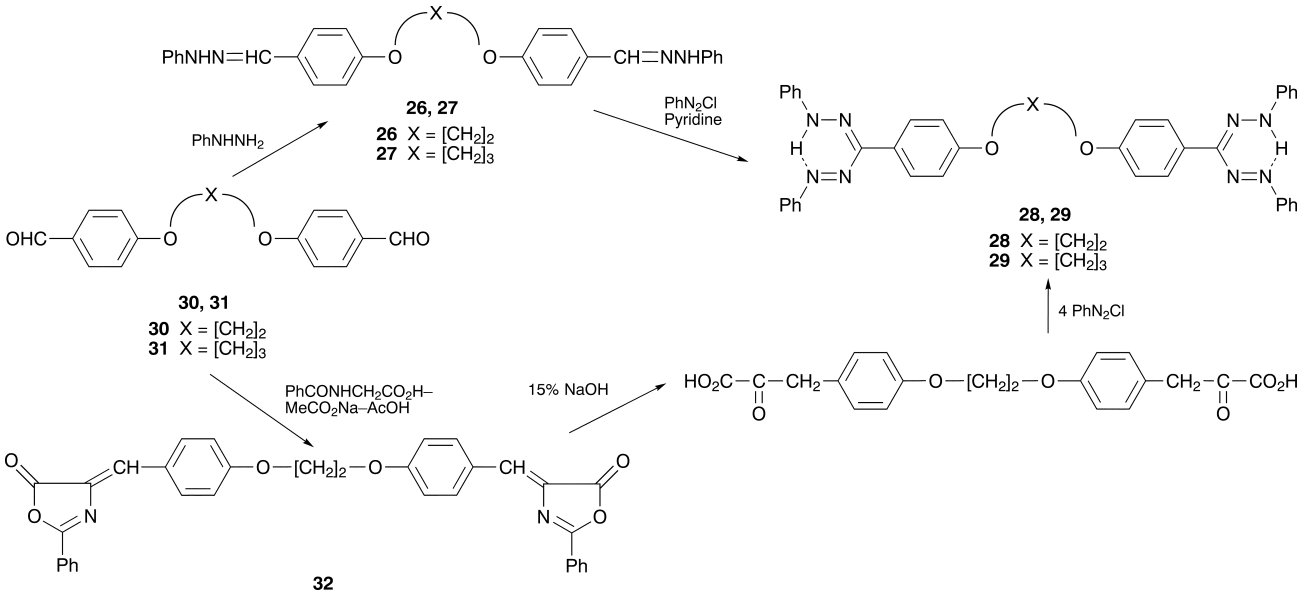

Scheme 2

from 1,2-bis(*p*-formylphenoxy)ethane **30** by converting it first to the bisarylpyruvic acid **33** (*via* the intermediate bisoxazolone **32**) followed by coupling with benzenediazonium chloride.

Finally compounds **15**–**17** and **21** were converted into the interesting new bisverdazyls **34–37** upon treatment with paraformaldehyde and boron trifluoride diethyl etherate in chloroform, followed by aqueous formaldehyde and then aqueous sodium hydroxide as reported.[33]

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Techniques used: ^{1}H and ^{13}C NMR, MS, ESR

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