Tetrahedron Letters Vol. 21, pp 3831 - 3834
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0040-4039/80/0922-3831$02.00/0

NOVEL FURAN DERIVATIVES RELATED TO TRIPHENYLENE: BENZO[1,2-*c*:3,4-*c*':5,6-*c*"]-TRIFURAN, NAPHTHO[1,2-*c*:3,4-*c*']DIFURAN AND PHENANTHRO[9,10-*c*]FURAN

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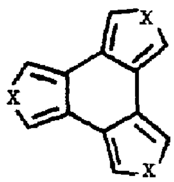
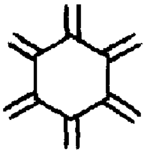
Abstract: The title compounds have been synthesised by sequences involving as the key step the trapping of arynes with furan.

Considerable interest has recently been shown in molecules represented by general structure *1*.[1-3] Such molecules may in one sense be formally regarded as heteroatom bridged derivatives of the highly reactive molecule hexaradialene *2*.[4] On the other hand, structure *1* may be viewed as a derivative of the stable aromatic molecule triphenylene *3*, in which the benzene rings have been replaced by *c*-fused 5-membered heterocycles. To date only two members of the heterocyclic series *1* have been reported: benzo[1,2-*c*:3,4-*c*':5,6-*c*"]trithiophene *1a*,[1] and N,N',N"-tribenzylbenzo[1,2-*c*:3,4-*c*':5,6-*c*"]tripyrrole *1b*.[2] An all carbocyclic derivative of *1*, the "trindene trianion" (*1*, X = CH$^-$) has also been generated.[3] In this note we report the preparation of benzo[1,2-*c*:3,4-*c*':5,6-*c*"]trifuran *1c* by a strategy involving sequential Diels-Alder additions of arynes to furan. We have also prepared molecules in which first one, and then two furan rings of *1c* are replaced by benzene rings.



1a X = S
1b X = NCH$_2$Ph
1c X = O



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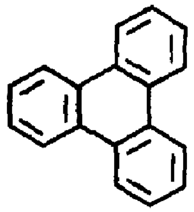

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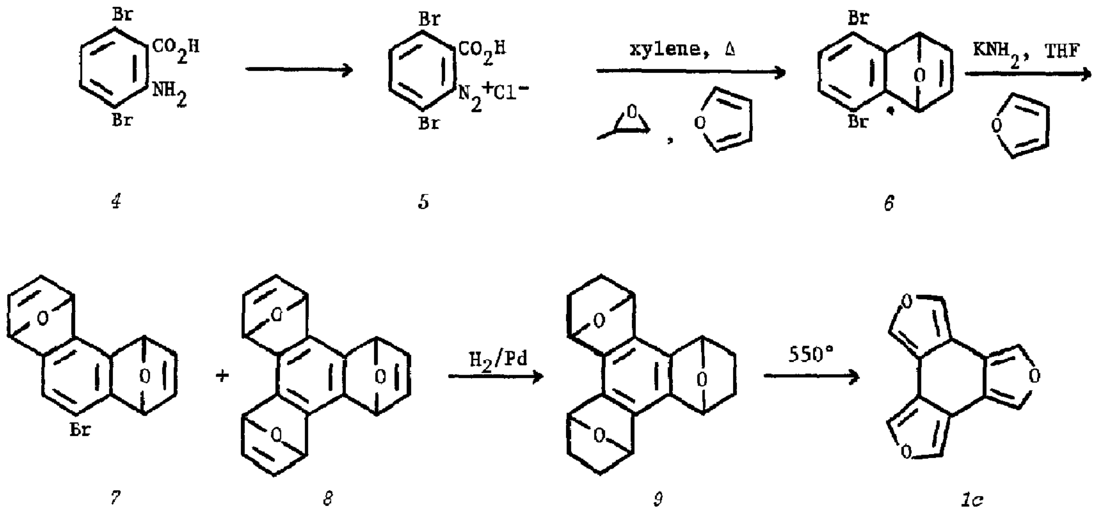
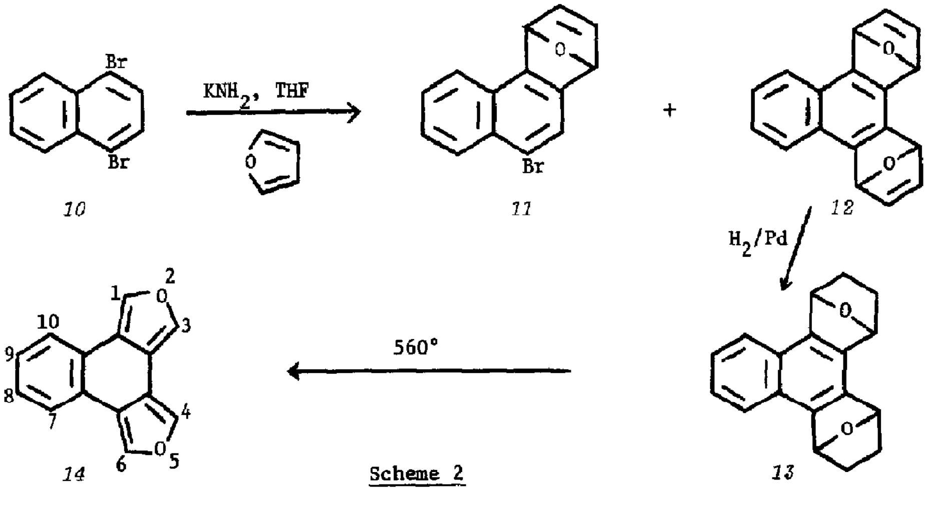
3,6-Dibromoanthranilic acid *4*[5] m.p. 149-51°, prepared from 2,5-dibromoaniline by a standard isatin synthesis, was converted into the diazonium hydrochloride *5*, which on thermal decomposition in the presence of furan afforded 5,8-dibromo-1,4-dihydro-1,4-epoxynaphthalene *6* (70%), m.p. 65-66.5°, ^{1}H n.m.r. (CDCl$_3$) δ 6.95 (s, 2H, vinyl), 6.76 (s, 2H, aromatic), 5.64 (s, 2H, bridgehead). Treatment of *6* with excess KNH$_2$ in refluxing THF containing furan as a trapping agent, followed by chromatographic separation over silica gel, gave in addition to unchanged[6] *6* (38%) the bromodiepoxytetrahydrophenanthrene *7* (42%) and the triepoxyhexahydrotriphenylene *8* (3%). The diepoxide *7* could be separated by careful chromatography over



Scheme 1

neutral Al_2O_3 into two isomers, corresponding to a syn and anti arrangement of the epoxide groups, but on presently available evidence we have been unable to make configurational assignments. Isomer *7a* had m.p. 199-202° (dec.), ^1H n.m.r. ($CDCl_3$) δ 7.01-6.84 (m, 5H, vinyl and aromatic), 5.78-5.56 (m, 4H, bridgehead), while isomer *7b* showed m.p. 125-135° (dec.), ^1H n.m.r. δ 7.04-6.74 (m, 5H, vinyl and aromatic), 5.85-5.57 (m, 4H, bridgehead). The isomer mixture was resubmitted to treatment with KNH_2 in THF furan to give, in addition to starting material (77%) the triepoxide *8* (11%) as colourless crystals, m.p. > 360°, ^1H n.m.r. ($CDCl_3$) δ 6.94-6.70 (m, 6H, vinyl), 5.76-6.65 (m, 6H, bridgehead), which on hydrogenation afforded *9* (100%), m.p. 272-4°, ^1H n.m.r. ($CDCl_3$) δ 5.46-5.39 (m, 6H, bridgehead), 2.14-1.98 (m, 6H, exo methylene), 1.57-1.08 (m, 6H, endo methylene). HPLC analysis showed that *9* consisted of two isomers in a *c* 2:1 ratio, corresponding to the two possible orientations of the epoxide bridges. Expulsion of ethylene via a retro-Diels-Alder reaction was carried out by subliming *9* through an unpacked silica tube at 550°/0.01 mm to give benzo[1,2-*c*:3,4-*c*':4,5-*c*"]trifuran *1c* as a colourless crystalline solid (100%), m.p. 189-190°, ^1H n.m.r. ($CDCl_3$) δ 7.79 (s); ^{13}C {^1H} ($CDCl_3$) δ 136.6 (α-furan C), 114.3 (β-furan C); electronic spectrum (cyclohexane) λ_{max} (log ε) 216(3.69), 222.5(3.72), 237sh(3.29), 249sh(2.92), 259(2.82), 278(2.32) nm.

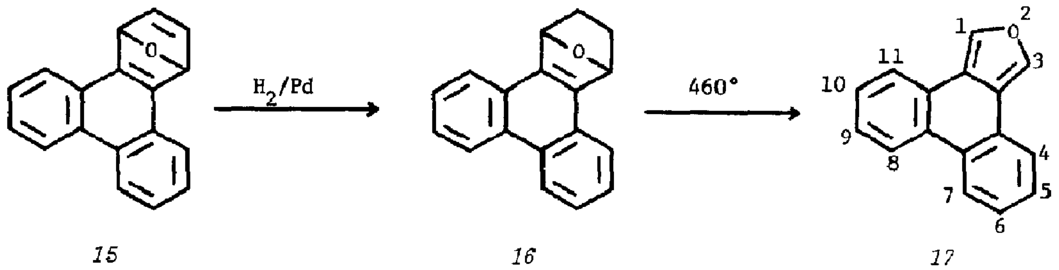
A similar strategy has been applied to the synthesis of naphtho[1,2-*c*:3,4-*c*']difuran *14* (Scheme 2). Thus heating 1,4-dibromonaphthalene *10* with KNH_2 in THF-furan gave 9-bromo-



Scheme 2

1,4-dihydro-1,4-epoxyphenanthrene *11* (33%), m.p. 115-16°, ^{1}H n.m.r. ($CDCl_3$) δ 8.27-8.06 (m, 1H, H5), 7.81-7.67 (m, 2H, H8, H10), 7.51-7.32 (m, 2H, H6, H7), 7.19-7.03 (m, H2, H3), 6.19 (brs, 1H, H4), 5.84 (brs, 1H, H1), together with 1,4:5,8-diepoxy-1,4,5,8-tetrahydrotriphenylene *12* as a mixture of syn and anti isomers. Isomer *12a* (15%) formed colourless crystals, m.p. 195-215° (dec.), ^{1}H n.m.r. ($CDCl_3$) δ 7.81-7.59 (m, 2H, H9, H12), 7.35-6.93 (m, 6H, H2, H3, H6, H7, H10, H11), 6.20-6.12 (m, 2H, H1, H8), 5.96-5.90 (m, 2H, H4, H5), while isomer *12b* (16%) had m.p. 148-157° (dec.), ^{1}H n.m.r. ($CDCl_3$) δ 7.82-7.61 (m, 2H, H9, H12), 7.36-6.96 (m, 6H, H2, H3, H6, H7, H10, H11), 6.21-6.14 (m, 2H, H1, H8), 6.05-6.00 (m, 2H, H4, H5). Catalytic hydrogenation of *12a* quantitatively gave *13a*, m.p. 185-6°, ^{1}H n.m.r. ($CDCl_3$) δ 7.95-7.75 (m, 2H, H9, H12), 7.53-7.32 (m, 2H, H10, H11), 5.96-5.88 (m, 2H, H1, H8), 5.66-5.58 (m, 2H, H4, H5), 2.34-1.92 (m, 4H, exo methylene), 1.57-1.15 (m, 4H, endo methylene), while hydrogenation of *12b* afforded *13b*, m.p. 253-4°, ^{1}H n.m.r. ($CDCl_3$) δ 7.93-7.73 (m, 2H, H9, H12), 7.53-7.33 (m, 2H, H10, H11), 5.96-5.87 (m, 2H, H1, H8), 5.70-5.60 (m, 2H, H4, H5), 2.26-1.98 (m, 4H, exo methylene), 1.42-1.08 (m, 4H, endo methylene). Sublimation of either stereoisomer *13* through a silica tube at 560°/0.01 mm quantitatively gave the naphthodifuran *14*, m.p. 114-15°, ^{1}H n.m.r. ($CDCl_3$) δ 7.97 (d, J 1.3Hz, 2H, H1, H6), 7.78 (d, J 1.3Hz, 2H, H3, H4), 7.80-7.59 (m, 2H, H7, H10), 7.35-7.16 (m, 2H, H8, H9); ^{13}C {^{1}H} n.m.r. ($CDCl_3$) δ 137.0, 136.4 (C1, C3, C4, C6), 127.3, 124.6 (C7, C8, C9, C10), 125.9 (C6b, C10a), 122.0, 113.9 (C3a, C3b, C6a, C10b); electronic spectrum (cyclohexane) λ_{max} (log ε) 218.5(4.16), 226(4.21), 233(4.31), 242(4.33), 263(3.95), 274(4.00), 285(3.95), 295sh(3.20), 306(3.08), 309sh(2.94), 320(2.97, 332(2.23) nm.

The third triphenylene analogue, phenanthro[9,10-*c*]furan *17* was prepared as shown in Scheme 3. The previously reported[7] epoxide *15* was obtained in 62% yield by heating 9-bromophenanthrene with $NaNH_2$ in THF-furan. Hydrogenation gave *16* (91%), m.p. 164°, ^{1}H n.m.r. ($CDCl_3$) δ 8.87-8.56 (m, 2H, H8, H9), 8.06-7.45 (m, 6H, other aromatic), 6.11-5.95 (m, 2H, bridgehead), 2.36-2.02 (m, 2H, exo methylene), 1.50-1.19 (m, 2H, endo methylene), which on thermolysis at 460°/0.1 mm followed by recrystallisation from deoxygenated pentane gave the furan *17* (95%), m.p. 102-3° (dec.), ^{1}H n.m.r. ($CDCl_3$) δ 8.38-8.21 (m, 2H, H7, H8), 8.16 (s, 2H, H1, H3), 7.95-7.78 (m, 2H, H4, H11), 7.50-7.28 (m, 4H, other aromatic); electronic spectrum (cyclohexane) λ_{max} (log ε) 238sh(4.24), 246(4.38), 252(4.38), 262(4.14), 292(3.56), 302(3.56), 317(3.34), 332(3.46) nm.



Scheme 3

A comparison of the electronic spectra of the furans *1c*, *14* and *17* (Figure) shows that as the furan rings are progressively replaced by benzene rings, the absorptions increase in intensity and assume more of the character of those of triphenylene. Unlike the trithiophene derivative *1a*,[1] the furan *1c* bears little electronic resemblance to triphenylene. This is readily understood in qualitative terms since furan possesses less aromatic character then thiophene.[8]

The furan derivatives *1c*, *14* and *17* may also be viewed as annellated derivatives of the highly reactive molecule isobenzofuran *18*.[9-11] We have used similar approaches to those outlined in Schemes 1-3 to prepare the furans *19*, *20* and *21*, and in these cases, as in *17* the annellation also is observed to qualitatively stabilise the isobenzofuran structural system. A quantitative study of the reactivity of all of these novel furan derivatives is in progress.

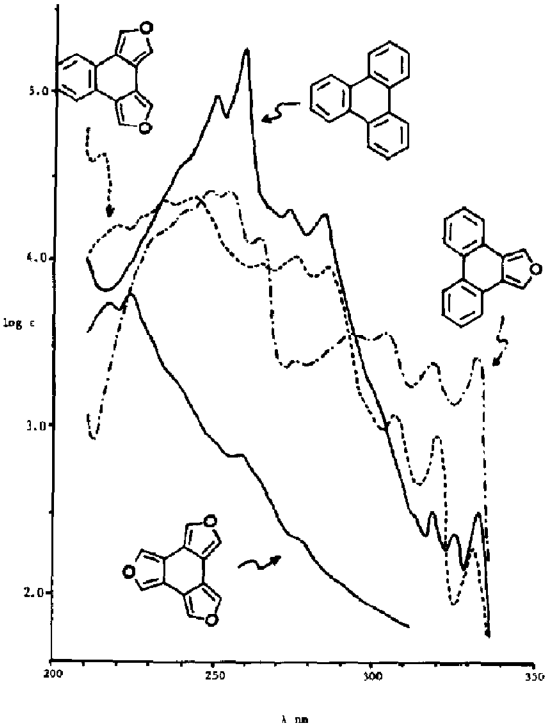
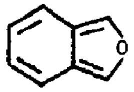


Figure. Electronic spectra of the furans *1c*, *14*, *17* and triphenylene in cyclohexane.



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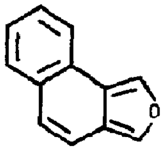

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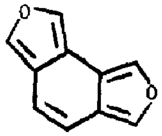

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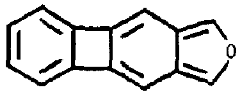

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Acknowledgement. We thank the Australian Research Grants Committee for financial support.

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(Received in UK 24 July 1980)