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THE SYNTHESIS OF SOME FURO[3,2-c]CARBAZOLYL PHOSPHONATES BY PHOSPHORUS DEOXYGENATION OF α,α,-DI(2-FURYL)-*o*-NITRO TOLUENES

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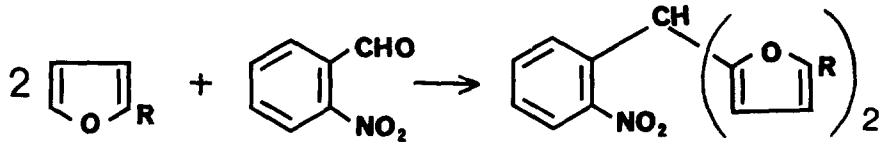
We have reported[1,2] a number of insertion reactions using o-azidodiphenylmethanes to obtain azepinoindoles or acridans. Similar nitrene insertions into thiophen rings gave products in which extensive reorganisation of the heterocyclic rings had occurred.[3] We have attempted to prepare o-azidobenzylfurans but have been unable to find satisfactory conditions for the crucial diazotisation of the precursor *o*-aminobenzylfurans. We have, however, prepared a number of α,α-di(2-furyl)-*o*-nitrotoluenes, (5) to (8); deoxygenation of these has given a route to a new heterocyclic system.



(1)	R = CH_3	(5)	R = CH_3 ,	50%
(2)	R = C_2H_5	(6)	R = C_2H_5 ,	47%
(3)	R = *t*-C_4H_9	(7)	R = *t*-C_4H_9,	75%
(4)	R = H	(8)	R = H ,	33%

The compounds (5) to (8) were prepared by acid catalysed condensation of *o*-nitrobenzaldehyde with the appropriate furan (1) to (4). Deoxygenation of the nitro compounds (5) by triethylphosphite in boiling cumene gave after chromatography a crystalline product, m.p. 80° (28% yield), of formula $C_{19}H_{20}NO_4P$.[3] The spectral evidence, particularly the ^1H n.m.r. spectrum (Fig.1) show that this is the first example of the furo[3,2-c]-carbazole series, the phosphonate (9). In the ^1H n.m.r. signal the signals from the two ethoxy groups are clearly seen, the subsplitting on the signal at δ4.1 being due to ^{31}P coupling; the phosphonate grouping is confirmed by a ^{31}P signal at -21 p.p.m. (from phosphoric acid). The methyl signal at δ2.55 is coupled to the single proton at δ6.42 and this has been noted previously with angularly fused five membered rings.[4] Most revealingly, the broad exchangeable NH signal at δ10.5 and a doublet (1H, J 14 Hz) at δ7.7 were shifted downfield by $Eu(fod)_3$, as were the methylene signals of the phosphonate

ethyl groups. Assuming complexing with the phosphonate by the $Eu(fod)_3$ this establishes the phosphonate at position 5. Similar compounds (10) and (11) were obtained from the ethyl and *tert*-butyl compounds (6) and (7), but no identifiable products from compound (8).

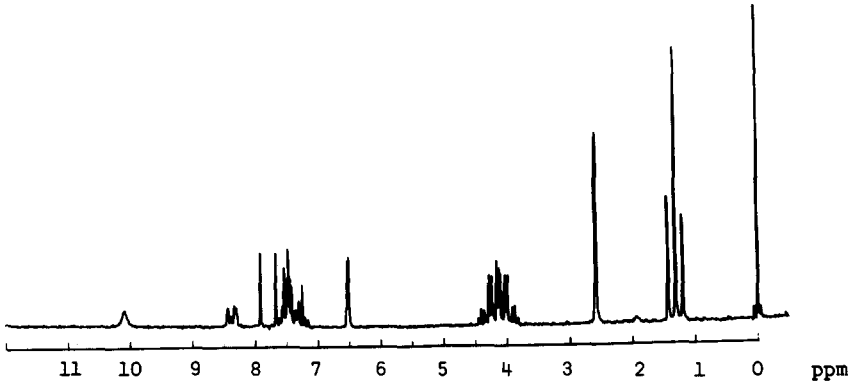
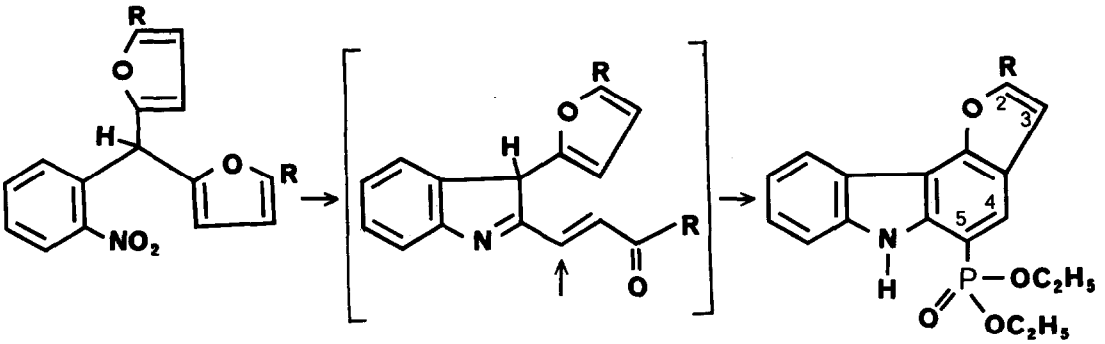


Figure: ^1H N.m.r. spectrum of diethyl 2-methylfuro[3,2-c]carbazolyl phosphonate (9)

The mechanism of formation of the furocarbazole phosphonates remains obscure. It is known[4-5] that nitrene insertion can rupture a furan ring, producing an α, β-unsaturated ketone as shown in intermediate (12); such an intermediate is well set up for addition of phosphite at the arrowed position, which will eventually be position 5 in the furocarbazole but as to the fate of the acyl fragment and the exact mechanism of the ring closure, no evidence is available. The only identified volatile fragment was acetaldehyde (as D.N.P.) from compounds (7) and (8).



(12)

(9) R = CH_3
(10) R = C_2H_5
(11) R = t-C_4H_9

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