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exo-3-AZA-3-PHENYLTRICYCLO[3,2,1,$0^{2,4}$]OCT-6-ENES

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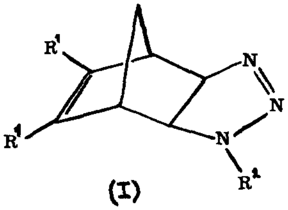
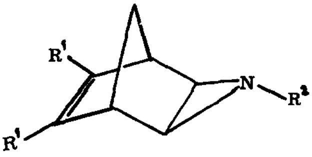
The 1,3-dipolar cyclo-additions of organic azides to strained cyclic olefins are well documented. Phenyl azide[1,2] and ethyl azidoformate[3] are known to undergo stereoselective addition to norbornadiene to give the corresponding *exo*-Δ^2-triazoline adducts (Ib,c), while phenylsulphonyl azide[4] affords only the unstable *exo*-3-azatricyclo-octene (IId). Although the parent azatricyclo-octene (IIa) has been prepared[3] no N-alkyl or N-aryl derivatives have been previously reported. We now report the synthesis of the *exo*-3-aza-3-phenyltricyclo [3,2,1,$0^{2,4}$]oct-6-enes (IIb,e).

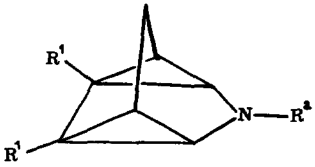
In an earlier communication McLean and Findlay reported that photolysis of (Ib) resulted in the formation of uncharacterisable tars together with some residual starting material.[2] Contrary to this report we find that photolysis of (Ib)[5a] results in the smooth elimination of molecular nitrogen and the formation of (IIb) in almost quantitative yield[6] [m.p. 38-39°; δ ($CDCl_3$) 1.48 (2H q J 9.0Hz), 2.39 (2H s), 2.91 (2H m), 6.23 (2H t J 2.0Hz), 6.95 (5H m)]. In like manner, photolysis of (Ie),[5b] prepared by addition of phenyl azide to



(I)



(II)



(III)

a) $R^1 = R^2 = H$ b) $R^1 = H$; $R^2 = Ph$ c) $R^1 = H$; $R^2 = CO_2Et$

d) $R^1 = H$; $R^2 = SO_2Ph$ e) $R^1 = CO_2Me$; $R^2 = Ph$

dimethyl norbornadiene-2,3-dicarboxylate, affords (IIe) although in considerably lower yield [40%; m.p. 111-113°; δ ($CDCl_3$) 1.80 (2H q J 9.0Hz), 2.84 (2H s), 3.51 (2H m), 3.79 (6H s), 7.10 (5H m)]. In contrast with the photochemical reaction, pyrolysis of (Ib)[1,2] or (Ie) above 100° results in the formation of 1-phenyl-1,2,3-triazole by a retrodiene reaction.

Suitable 3-azatricyclo-octenes (II) could be expected to undergo internal $[{}_{\pi}2_s + {}_{\sigma}2_s]$ photocyclo-addition to the corresponding 3-azatetracyclo$[3,2,1,0^{2,7},0^{4,6}]$octanes (III), as has been demonstrated recently by Klaus and Prinzbach for trimethyl *exo*-3-azatricyclo$[3,2,1,0^{2,4}]$oct-6-ene-3,6,7-tricarboxylate.[7] Our preliminary results with (IIb) and (IIe) are in accord with this, but the cyclo-addition products obtained revert thermally to the starting materials, further details of which will be published in a subsequent paper.

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References and Footnotes:

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2. S. McLean and D.M. Findlay, *Tetrahedron Letters*, 2219, 1969.
3. K. Tori, K. Kitahonoki, Y. Takano, H. Tanida and T. Tsuji, Tetrahedron Letters, 869, 1965.
4. A.C. Oehlschlager and L.H. Zalkow, *J. Org. Chem.*, **30**, 4205, 1965.
5. Photolyses were performed in a Rayonet RPR 204 preparative photochemical reactor (a) at 300nm (b) at 350nm.
6. Satisfactory microanalytical and spectral data were obtained for all new compounds reported.
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