

A Mild Retro- $[\pi 4_s + \pi 2_s]$ Cleavage Route to Furans and Fulvenes

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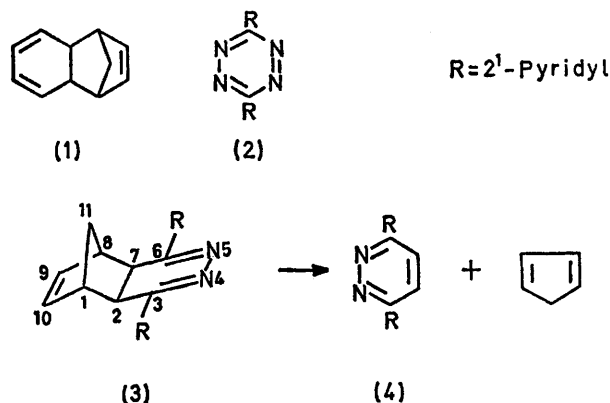
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Summary A new route to β -substituted furans and fulvenes has been developed which is based on the ready thermal fragmentation of 4,5-diazatricyclo[6,2,1,0^{2,5}]-undeca-3,5,9-trienes.

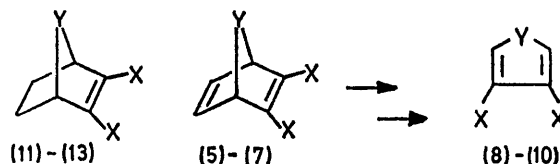
RETRO- $[\pi 4_s + \pi 2_s]$ (Diels-Alder) reactions are commonly used in synthesis.¹ These reactions are conducted under thermal conditions and extreme temperatures are often required to effect fragmentation.¹ This is one limitation where temperature sensitive products are the goal,² although this has been partly offset by flash vacuum pyrolysis techniques. This latter technique is elegantly demonstrated by the recent report by de Mayo and his co-workers on the synthesis of pentalene.³

We⁴ and others⁵ have observed that derivatives of the tricyclo[6,2,1,0^{2,5}]undeca-3,5,9-triene system (**1**) are particularly labile in respect to retro- $[\pi 4_s + \pi 2_s]$ cleavage, especially when the $\pi 2_s$ component becomes part of an aromatic system. We have now developed a scheme for the synthesis of β -substituted furans and fulvenes which is based on the fragmentation of the 4,5-diaza-analogue of (**1**). The features of this scheme are: (i) simple formation of the diaza-intermediate, (ii) low temperatures involved, especially in the fragmentation step, (iii) essentially quantitative conversions in each step.

In order to evaluate the stability of the 4,5-diazatricyclo[6,2,1,0^{2,5}]undeca-3,5,9-triene system, the 3,6-di-(2'-pyridyl) derivative (**3**) was prepared from the reaction of equimolar



the literature.^{2,6} The standard method involves the following steps: (a) Formation of bicyclic adduct, (5)—(7); (b) Selective hydrogenation to the dihydro-derivative (11)—(13); (c) High temperature pyrolysis (195—400°) to the 5-membered product (8)—(10) plus ethylene.



Reaction of the 7-substituted norbornadienes (5)—(7) readily occurred with the *s*-tetrazine (2) under mild con-

TABLE

Summary of conditions for conversion of 7-substituted norbornadienes into furans and fulvenes

Substituents X	Y	Dihydro- compound	Starting material	Reaction conditions	Product	¹ H n.m.r. (δ p.p.m.) ^a of product
CF ₃	O	(11)	(5)	room temp., CDCl ₃ few h	(8) ^b	7.90 (s, vinylic)
CO ₂ Me	C=CPh ₂	(12)	(6)	room temp., CDCl ₃ overnight	(9) ^c	7.35—7.65 (m, phenyl) 6.97 (s, vinylic) 3.85 (s, OMe)
CO ₂ Me	C=CMc ₂	(13)	(7)	50°, CDCl ₃ 2 h	(10) ^d	7.16 (s, vinylic) 3.83 (s, OMe) 2.31 (s, Me)

^a 60 MHz, CDCl₃, MeSi as internal standard. ^b Low boiling liquid, isolated by g.l.p.c. (carbowax 20M, fluoroport, 58°) (*m/e* 204). ^c M.p. 166°, reported² 165—167°, isolated by preparative layer chromatography (silica, CHCl₃) (*m/e* 350). ^d Unstable low-melting solid, isolated by short path distillation (*m/e* 222).

amounts of 3,6-di-(2'-pyridyl)-*s*-tetrazine and norbornadiene in CDCl₃ at -20°. A rapid reaction occurred and nitrogen was eliminated to yield (3) in quantitative yield [¹H n.m.r., δ 1.19, 1.28 (2H, AB q, *J* 9 Hz, 11-H₂), 3.40 (2H, m, 1-, 8-H), 3.54 (2H, s, 2-, 7-H), 6.50 (2H, t, 9-, 10-H), 7.3—8.90 p.p.m. (8H, complex m, pyridyl)]. The lack of coupling between C-2(7) and C-1(8) supported the suggested stereochemistry, and is consistent with the *s*-tetrazine approaching from the less hindered *exo*-side. Intermediate (3) was stable below -10°, but above this temperature fragmentation to 3,6-di-(2'-pyridyl)pyridazine (4) and cyclopentadiene occurred.

In order to compare our method with the standard retro-[$\pi 4_s + \pi 2_s$] route used in synthesis of fulvenes³ and furans,⁶ we have chosen three reactions already reported in

ditions (see Table) to produce the corresponding 5-membered products (8)—(10) plus the pyridazine (4). ¹H N.m.r. spectroscopy showed that the conversions were quantitative, although the isolated yields were only in the range 70—90%. The spectral properties of the products were in agreement with the assigned structures (see Table). Dimethyl 6,6-dimethylfulvene-2,3-dicarboxylate was only moderately stable, and this would account for the lack of success reported by Alder and Trimborn³ using the standard retro-[$\pi 4_s + \pi 2_s$] route in attempts to prepare this product.

The generality of this method is demonstrated by the synthesis of isobenzofuran,⁷ isobenzofulvenes,^{8a} and isindoles.^{8b}

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⁸ Unpublished results: (a) P. L. Watson and R. N. Warrener; (b) G. M. Priestley and R. N. Warrener.