Nitrophenylcarbenes. Generation and Reactions with *cis*-Butene

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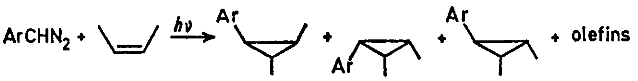
Summary A number of nitrophenylcarbenes, generated by the photolysis of the corresponding diazo-compounds, were found to add non-stereospecifically to *cis*-butene.

CONSIDERABLE interest has been shown in arylcarbenes especially in connection with their singlet–triplet reactivity.[1–4] I report the non-stereospecific addition of a number of nitrophenylcarbenes with *cis*-butene.

Previous attempts to generate 4-nitrophenylcarbene by α-elimination have failed to give any trapping product with olefins.[5,6] The carbene and a few other methyl-substituted analogues are now found to be conveniently generated by the photolyses of the diazo-compound precursors. A typical reaction was conducted by irradiating (500 W tungsten filament lamp or 300 W sunlamp) a solution of the aryldiazomethane, *cis*-butene, and benzene in a Pyrex reaction vessel which was cooled (10—15 °C) by circulating cold water. Photolysis was carried out for 4 h or to about 50% completion and the products, after chromatography through alumina, were isolated by g.l.c. The products consisted of cyclopropane adducts (*ca.* 30% yield) and some olefin insertion products 10—20% of the total.



(1) (2) (3)

The high percentage of non-stereospecific adducts (Table) is in contrast to the 3% non-stereospecificity observed for phenylcarbene.[8] Non-stereospecificity of the addition is usually attributed to the involvement of triplet states,[9] but although aryl- and diarylcarbenes in general have triplet ground states not all add to olefins.[1,2] A number of arylcarbenes[8] in fact undergoes highly stereospecific addition to *cis*- and *trans*-butene, the result being attributed to the singlet state reaction although a very fast ring closure of the intermediate trimethylene diradical (due to a triplet state reaction) cannot be ruled out.

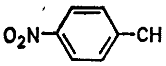
The nitro-group may affect non-stereospecificity of addition in various ways. First, increased electron delocalization (hence, stabilization) by the nitro-substituent can enhance triplet state formation (the zero-field parameter D from e.s.r. spectra of 4-nitrophenyl carbene is 0·480 cm^{-1} compared to 0·518 cm^{-1} for phenylcarbene).[10] Secondly, stabilization of the trimethylene diradical intermediate by the nitro-group can increase its life-time, allowing greater bond rotation which gives rise to a larger amount of non-stereospecific addition. Thirdly, nitro-groups are known to enhance singlet–triplet intersystem crossing[11] which can occur either in the carbene or in the diazo-compound precursor. This is evident in *m*-nitrophenylcarbene where although odd-electron delocalization to the nitro-group is not possible, 17% *non*-stereospecificity was observed. The second factor must also be of some importance since triplet phenylcarbene[1] has been observed to give mainly insertion products and the non-stereospecific addition amounted only to a maximum of 7%.

TABLE

Addition of nitrophenylcarbenes to cis-*butene*

Carbene	%Nonstereospecificity[a]	Cyclopropylmethyl protons (δ in p.p.m.)[b]		
		(1)	(2)	(3)
(4)	60	0·88, 1·22	0·95	1·23
(5)	47	0·84, 1·19	0·96	1·20
(6)	35	0·83, 1·16	0·97	1·15
(7)	40	0·72, 1·25	1·01	1·24
(8)	17[c]	0·82, 1·24	0·98	1·23

[a] Percentage of non-stereospecific cyclopropane of the total cyclopropane products. [b] In CCl_4 solutions, p.p.m. downfield from internal Me_4Si. [c] From ref. 7.



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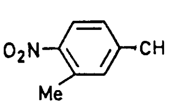

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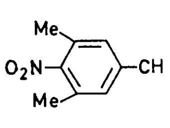

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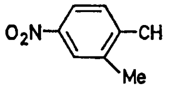

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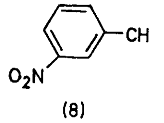

(8)

The effect of the substitution of methyl groups in the carbenes is to decrease non-stereospecificity (Table); in the case of the di-*o*-substituted nitrophenylcarbene which exhibited the lowest non-stereospecificity, a steric effect may be in operation. This is not unexpected since *o*-substitution of nitro-compounds is known to reduce the conjugation of the nitro-group with the ring.[12]

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