

## Reactivity of Triplet-state Nitrophenylcarbenes towards *cis*-Butene

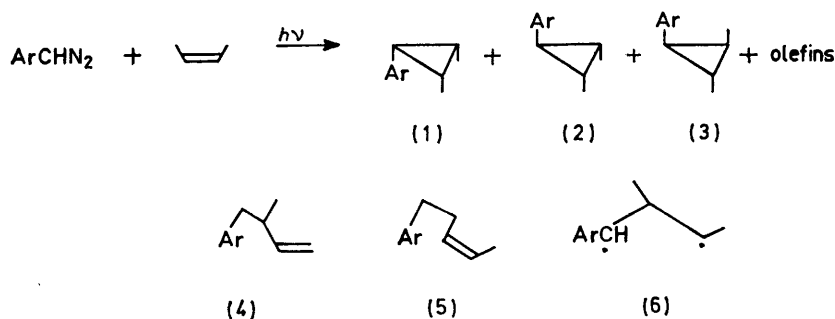
By Swee Hock Goh\* and Hooi Long Gian, Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

A series of nitrophenylcarbenes ArCH (Ar = 3-Me-4-O<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>, 3,5-Me<sub>2</sub>-4-O<sub>2</sub>NC<sub>6</sub>H<sub>2</sub>, 2-Me-4-O<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>, and 2-Me-5-O<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>), generated photolytically, was found to insert as well as add (non-stereospecifically) to a high degree to *cis*-butene. Results indicate that both *m*- or *p*-nitro-substituents enhance triplet populations. Further methyl substitution, however, can enhance or reduce triplet populations if substituted *ortho* to the carbene centre or nitro-group, respectively.

ARYLCARBENES have triplet ground states<sup>1</sup> but the usual rule of non-stereospecific addition to olefins may not be observed; for example, arylcarbenes generated photolytically from different sources react mainly in the singlet state.<sup>2-6</sup> While the photolytic decomposition of  $\alpha$ -diazotoluene solution in simple olefins leads to mainly stereospecific cyclopropanation (>97%),<sup>2-5</sup> significant non-stereospecific addition had been observed, however, by irradiating the diazo-compound in frozen *cis*-but-2-ene.<sup>5</sup> Although the reasons for such observations in studies at low temperature may not be exactly known, a simple explanation has been offered that the non-stereospecific addition observed at low temperatures is the consequence of a longer lifetime which allows the first reacting species, *i.e.* singlet, to convert by inter-system crossing to the triplet ground state.

The diazo-compounds were stable at 0 °C and were readily obtained as reddish orange crystals which had characteristic i.r. and n.m.r. spectra. Irradiation of these carbene precursors in *cis*-but-2-ene was carried out in a Pyrex vessel and cyclopropanation products (1)—(3) as well as olefins were formed.

The three cyclopropanation adducts (1)—(3) were identified by n.m.r. and g.l.c.-mass spectroscopy. The stereochemistry of the *syn*- and *anti*-isomers of *cis*-dimethylcyclopropanes (1) and (2) were assigned by <sup>1</sup>H n.m.r. spectroscopy according to the method of Closs and Moss.<sup>3</sup> The stability of the cyclopropanes to the reaction conditions was tested by subjecting a known mixture of the synthetic cyclopropylbenzenes to the same conditions as in photolyses. Most of the nitrophenylcyclopropanes do not isomerize significantly



The earlier study by Closs and Moss<sup>3</sup> showed that though arylcarbenes are triplet ground states their reactions with olefins are indicative of that of the first formed singlet states. [Thus, for a number of substituted arylcarbenes the amount of non-stereospecific addition to *cis*-butene amounted to not more than 5%.

Nitrophenylcarbenes, however, are of interest because the nitro-substituent appears to exert a marked effect on the reactivity of the carbene. In an earlier communication<sup>7</sup> it was found that some nitrophenylcarbenes as prepared by irradiation of the corresponding diazo-compounds in olefin solution add to *cis*-but-2-ene with a high degree of non-stereospecificity. The present paper details some of the findings of the study of this series of nitrophenylcarbenes.

### RESULTS AND DISCUSSION

The series of diazo-compounds were prepared by oxidation of the corresponding hydrazones with activated

(<6%) in benzene or ethyl acetate solutions except for *syn*-1-(2-methyl-4-nitrophenyl)-*cis*-2,3-dimethylcyclopropane (1) which was found to isomerize to *ca.* 40% to the *trans*-dimethyl isomer (3). The olefins were detectable as two peaks in the gas chromatogram and were assumed to be mainly (4) and (5), by analogy to the reaction of 4-nitrophenylcarbene studied earlier in detail.<sup>5</sup> These olefins were removed by bromination at low temperature so that the cleaner gas chromatogram allowed the percentages of the three isomeric cyclopropanes to be determined.

As shown in Table 1 the percentages of the non-stereospecific cyclopropanation products of nitroarylcarbenes in the present study are significantly greater than those observed for phenylcarbene and other substituted phenylcarbenes.<sup>5</sup> Since non-stereospecificity in the carbene addition to olefins is usually attributed to the involvement of the triplets, the above results may partly be the result of enhanced triplet formation through

TABLE 1  
Reactions of nitrophenylcarbenes with *cis*-butene

Phenyl substituents	% Non-stereospecificity <sup>b</sup>	% Olefins	Cyclopropylmethyl protons ( $\delta$ ) <sup>a</sup>		
			<i>trans</i> (3)	<i>syn</i> (1)	<i>anti</i> (2)
4-Nitro	60 <sup>c</sup>	21	0.88, 1.22	0.95	1.23
3-Methyl-4-nitro	47	17	0.84, 1.19	0.96	1.20
3,5-Dimethyl-4-nitro	35	17	0.83, 1.16	0.96	1.16
2-Methyl-4-nitro	64	30	0.74, 1.22	0.98	1.23
3-Nitro	17 <sup>c</sup>	6	0.82, 1.24	0.98	1.23
2-Methyl-5-nitro	40	22	0.72, 1.25	1.01	1.24

<sup>a</sup> Percentage of non-stereospecific cyclopropane adduct (3) of the total cyclopropane products. <sup>b</sup> In  $\text{CCl}_4$  solutions, p.p.m. downfield from internal  $\text{Me}_4\text{Si}$ . <sup>c</sup> From ref. 7.

resonance stabilization by the nitro-groups. Moreover, the nitro-groups are known to promote singlet-triplet intersystem crossing<sup>8</sup> to the triplet ground state. This is probably responsible for the 17% non-stereospecificity observed in 3-nitrophenylcarbene where the odd electron delocalization to the nitro-substituent is not possible. However, it is not possible to deduce from the present results whether the intersystem crossing occurs in the diazo-precursors or in the carbenes or both. Noteworthy also is the fact that the yields of cyclopropane adducts are relatively high as compared to other triplet arylcarbenes. This must be due to the higher electrophilicity of nitrophenylcarbenes.

An additional and perhaps the more important factor responsible for the high degree of non-stereospecificity is resonance stabilization of the trimethylene diradical intermediate (6) involved in the triplet carbene addition to olefins. With longer lifetime and hence greater bond rotation, the diradical tends to form a larger amount of non-stereospecific adduct. This is evident in the high non-stereospecificity displayed by 4-nitrophenylcarbene in its addition to *cis*-but-2-ene. In the cyclopropanation of 3,5-dimethyl-4-nitrophenylcarbene, the amount of non-stereospecific adducts formed is expected to be lower because of the steric inhibition to the nitro-group by the two adjacent methyl groups. Even the presence of a single *o*-methyl group is sufficient to cause steric hindrance to the nitro-group, with a concomitant increase in stereospecificity. The greatest extent of non-stereospecific addition by 2-methyl-4-nitrophenylcarbene in the series (Table 1) is not unexpected. With a blocking methyl group adjacent to the carbenic carbon, a relatively longer lived carbene may be possible and likewise the cyclization of the trimethylene diradical (6) will be hindered; a longer lifetime of the intermediate thus allows greater bond rotation.

In addition to the non-stereospecific cyclopropanation adducts, the triplet-state carbene reactions also give rise to significant amounts of olefinic insertion products *via* the abstraction-recombination process. It is likely that arylcarbenes when generated photolytically are in

a non-equilibrium of singlet and triplet states so that the products as observed have to be attributed to both species. The insertion products as may be expected arise from the triplet species and it is also apparent that there is a corresponding increase of insertion accompanying the increase of non-stereospecificity. Noteworthy is the result for 2-methyl-5-nitrophenylcarbene, though a *m*-nitro-substituted phenylcarbene, shows a relatively large amount of non-stereospecific addition and insertion products. The larger reacting triplet population must be the result of lowered reactivity due to the steric hindrance by the *o*-methyl group.

#### EXPERIMENTAL

All m.p.s and b.p.s are uncorrected. I.r. spectra were recorded on a Beckman IR 12 or 4240 spectrometer. <sup>1</sup>H N.m.r. spectra were obtained with a Perkin-Elmer-Hitachi R20 instrument. An AEI MS3074 mass spectrometer was used to record mass spectra and g.l.c.-m.s. Product distributions were determined with a Varian Series 1800 and a Tracor 560 gas chromatograph, both equipped with flame ionization detectors. Preparative g.l.c. was performed on a Varian series 1520 instrument equipped with a thermal conductivity detector. Quantitation of products was performed on a 8 ft 6% OV-17 and a 12 ft 10% DC-550 columns. Preparative columns used were 12 ft 10% DC-550, 10 ft 15% SE-30, and 12 ft 20% QF-1 columns.

*cis*-But-2-ene was obtained from Fluka and contained >99% of the *cis*-isomer.

*Preparation of Methyl-substituted Nitrobenzaldehydes.*—3-Methyl-4-nitrobenzaldehyde and 3,5-dimethyl-4-nitrobenzaldehyde were prepared as described previously.<sup>9</sup> 2-Methyl-5-nitrobenzaldehyde was similarly prepared by oxidizing 3,4-dimethylnitrobenzene and subsequently hydrolysing the diacetate formed. *Ca.* 15% 2-methyl-4-nitrobenzaldehyde was also formed in this preparation.

3-Methyl-4-nitrobenzylidene diacetate (65%) had m.p. 87–89 °C (lit., 86.5–88.5,<sup>9</sup> 80–82 °C<sup>10</sup>);  $\delta(\text{CDCl}_3)$  2.16 (6 H, s, 2 × Ac), 2.61 (3 H, s, Me), 7.3–7.6 (2 H, m, ArH), 7.66 (1 H, s, ArCH), and 7.77 (1 H, d, *J* 9 Hz, ArH).

3-Methyl-4-nitrobenzaldehyde (60%) had m.p. 59–62 °C (lit., 66–68,<sup>9</sup> 64 °C<sup>10</sup>);  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1 705 (C=O), 1 520, and 1 340  $\text{cm}^{-1}$  ( $\text{NO}_2$ );  $\delta(\text{CCl}_4)$  2.68 (3 H, s, Me), 7.7–8.1 (3 H, m, ArH), and 10.4 (1 H, s, CHO).

3,5-Dimethyl-4-nitrobenzylidene diacetate (38%) crystallized from ethanol, m.p. 128–129 °C (lit.,<sup>9</sup> 128–130 °C);  $\delta(\text{CCl}_4)$  2.08 (6 H, s, 2 × Ac), 2.32 (6 H, s, 2 × Me), 7.18 (2 H, s, ArH), and 7.40 (1 H, s, ArCH).

3,5-Dimethyl-4-nitrobenzaldehyde (38%) formed pale yellow needles from ethanol, m.p. 51–53 °C (lit.,<sup>9</sup> 52–54 °C);  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1 710 (C=O), 1 535, and 1 366  $\text{cm}^{-1}$  ( $\text{NO}_2$ );  $\delta(\text{CCl}_4)$  2.48 (6 H, s, 2 × Me), 7.56 (2 H, s, ArH), and 9.91 (1 H, s, CHO).

2-Methyl-5-nitrobenzylidene diacetate (60%) had m.p. 123–125 °C;  $\delta(\text{CCl}_4)$  2.15 (6 H, s, 2 × Ac), 2.35 (3 H, s, Me), 7.35 (1 H, d, *J* 8 Hz, ArH), 7.72 (1 H, s, ArCH), 8.12 (1 H, dd, *J* 8 and 2.5 Hz, ArH), and 8.37 (1 H, d, *J* 3 Hz, ArH).

2-Methyl-5-nitrobenzaldehyde (65%) formed needles from ethanol, m.p. 49–51 °C (lit.,<sup>11</sup> 55 °C);  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1 720 (C=O), 1 525, and 1 345  $\text{cm}^{-1}$  ( $\text{NO}_2$ );  $\delta(\text{CCl}_4)$  2.45 (3 H, s, Me), 7.38 (1 H, d, *J* 9 Hz, ArH), 8.22 (1 H, dd, *J* 9

and 2 Hz, ArH), 8.52 (1 H, d,  $J$  2 Hz, ArH), and 10.23 (1 H, s, CHO).

2-Methyl-4-nitrobenzaldehyde was prepared by the Sommelet reaction<sup>12</sup> of crude 2-methyl-4-nitrobenzyl bromide which, in turn, was prepared by bromination of 3,4-dimethylnitrobenzene with *N*-bromosuccinimide (NBS).<sup>13</sup>

**Bromination of 3,4-Dimethylnitrobenzene.**—NBS was dried by standing over phosphorus pentoxide in the desiccator while carbon tetrachloride was refluxed over  $P_2O_5$  for one day before distilling through a fractionating column. Dried NBS (0.4 mol) and dibenzoyl peroxide (0.8 g) were added to a solution of 3,4-dimethylnitrobenzene (0.4 mol) in  $CCl_4$  (240 ml). The mixture was heated under reflux for ca. 7 h. The crude products were filtered and the solvent was removed from the filtrate by rotary evaporation. The n.m.r. spectrum of the crude product showed that all the 3,4-dimethylnitrobenzene had been consumed and the major product, 2-methyl-4-nitrobenzyl bromide, showed a singlet at  $\delta$  4.45.

addition, the mixture was refluxed for a further 10 min and then cooled to give yellow or orange needles of the hydrazone in 40–62% yields (Table 2). In some cases, water was added to the cooled mixture to accelerate crystallization.

**General Method for the Preparation of Diazoalkanes.**—A mixture of activated manganese dioxide (0.08 mol) and the required hydrazone (0.02 mol) in  $CH_2Cl_2$  (ca. 100 ml) was stirred at 0 °C for 2–4 h (at room temperature in the preparation of  $\alpha$ -diazo-2-methyl-4-nitrotoluene). The black solids were filtered off and the filtrate was evaporated *in vacuo*. The red solid residue was extracted with *n*-hexane (benzene was used in extracting  $\alpha$ -diazo-2-methyl-4-nitrotoluene). Reddish orange crystals of the diazoalkane formed on cooling the combined extracts. The yields varied from 50 to 70% (Table 3).

**Photolysis of the Diazoalkanes in *cis*-But-2-ene.**—The diazo-compound (10 mmol) was dissolved in benzene (ca. 50 ml) in a Pyrex vessel which was cooled by an outer jacket of circulating cold water (ca. 10 °C) and fitted with a dry-ice

TABLE 2  
Analysis and spectral data of hydrazones

Hydrazone	M.p. (°C)	Elemental analysis (%) *			$\nu_{max.}/cm^{-1}$	$\delta(CDCl_3)$
		C	H	N		
3-Methyl-4-nitrobenzaldehyde	69—70	Found: 53.9	4.95	23.8	1 580,	2.61 (3 H, s, Me), 5.80br (2 H, s, $NNH_2$ ), 7.3—7.5 (2 H, m, ArH), 7.68 (1 H, s, ArCH), 7.97 (1 H, d, $J$ 9 Hz, ArH)
		(Calc.: 53.55	5.05	23.5	1 510,	
					1 340	
3,5-Dimethyl-4-nitrobenzaldehyde	62—63	Found: 55.7	6.1	21.85	1 590,	2.28 (6 H, s, 2 $\times$ Me), 5.62br (2 H, s, $NNH_2$ ), 7.26 (2 H, s, ArH), 7.57 (1 H, s, ArCH)
		(Calc.: 55.9	5.75	21.85)	1 520,	
					1 360	
2-Methyl-5-nitrobenzaldehyde	141—142	Found: 53.5	5.0	23.6	1 595,	2.48 (3 H, s, Me), 5.80br (2 H, s, $NNH_2$ ), 7.27 (1 H, d, $J$ 9 Hz, ArH), 7.93 (1 H, s, ArCH), 7.98 (1 H, dd, $J$ 9, 2 Hz, ArH)
		(Calc.: 53.55	5.05	23.55)	1 515,	
					1 345	
2-Methyl-4-nitrobenzaldehyde	124—125	Found: 54.0	5.15	23.55	1 580,	2.49 (3 H, s, Me), 5.85br (2 H, s, $NNH_2$ ), 7.85—8.05 (4 H, m, ArH and ArCH), 8.54 (1 H, d, $J$ 2 Hz, ArH)
		(Calc.: 53.55	5.05	23.55)	1 510,	
					1 340	

\* All elemental analyses were done by CSIRO, Australia.

**Preparation of 2-Methyl-4-nitrobenzaldehyde by the Sommelet Reaction.**—The crude 2-methyl-4-nitrobenzyl bromide was lachrymatory and was used without further purification. A mixture of the bromide and hexamine (0.6 mol) in 50% acetic acid (200 ml) was heated under reflux for 2 h. At the end of the reflux period, concentrated HCl (120 ml) was added and refluxing continued for 15 min to hydrolyse and destroy Schiff's bases which otherwise would contaminate the product. The resultant black mixture was extracted four times with 50 ml portions of diethyl ether. The combined extracts were neutralized with sodium carbonate, washed with water, dried, and evaporated. The n.m.r. spectrum of the residue showed the presence of two aldehydes with 2-methyl-5-nitrobenzaldehyde present as a minor product (ca. 15%). The separation of the two isomers was effected by column chromatography on silica gel. 2-Methyl-4-nitrobenzaldehyde was obtained as crystals from ethanol in 34% yield.

2-Methyl-4-nitrobenzaldehyde had m.p. 66—68 °C;  $\nu_{max.}$  ( $CCl_4$ ) 1 710 (C=O), 1 525, and 1 345  $cm^{-1}$  ( $NO_2$ );  $\delta(CDCl_3)$  2.26 (3 H, s, Me), 7.7—8.3 (3 H, m, ArH), and 10.32 (1 H, s, CHO).

**General Procedure for the Preparation of Hydrazones.**—The required aldehyde (0.1 mol) in absolute ethanol was added dropwise to a refluxing solution of hydrazine hydrate (98—99%; 0.8 mol) in absolute ethanol. After complete

condenser. *cis*-Butene (ca. 20 ml) was condensed into the mixture which was then irradiated by a 300 W sunlamp for 4—6 h. The photolysis was not complete after this period and unchanged diazo-compound was removed by passing

TABLE 3  
Spectral data of diazo-compounds

Diazo-compound	$\nu_{max.}(CH_2Cl_2)/cm^{-1}$	$\delta(CDCl_3)$
$\alpha$ -Diazo-3-methyl-4-nitrotoluene	2 065	2.61 (3 H, s, Me), 5.05 (1 H, s, ArCH), 7.7—8.2 (3 H, m, ArH)
$\alpha$ -Diazo-3,5-dimethyl-4-nitrotoluene	2 060	2.26 (6 H, s, 2 $\times$ Me), 4.85 (1 H, s, ArCH), 6.51 (2 H, s, ArH)
$\alpha$ -Diazo-2-methyl-5-nitrotoluene	2 060	2.24 (3 H, s, Me), 4.98 (1 H, s, ArCH), 7.18 (1 H, d, $J$ 8 Hz, ArH), 7.6—7.9 (2 H, m, ArH)
$\alpha$ -Diazo-2-methyl-4-nitrotoluene	2 060	2.22 (3 H, s, Me), 5.04 (1 H, s, ArCH), 6.90 (1 H, dd, $J$ 7, 2 Hz, ArH), 7.9—8.2 (2 H, m, ArH)

through a short column of alumina and the crude product was eluted with *n*-hexane. After removal of the solvent by rotary evaporation, the product was purified by vacuum distillation before being analysed by g.l.c. Olefinic products were detected by g.l.c. and g.l.c.—m.s. single ion  $M^+$

monitoring and then were removed by reaction with bromine at  $-10^{\circ}\text{C}$  so that a cleaner gas chromatogram could be obtained. Cyclopropanes were separated by preparative g.l.c. and identified by n.m.r. and mass spectroscopy. The yields of cyclopropane adducts and olefinic products range from 40 to 60% based on the diazo-compound precursor.

*Stability of the Cyclopropane Adducts under Photolysis Conditions.*—A known mixture of the *syn*- and *anti*-isomers synthesized as described previously<sup>4</sup> was dissolved in benzene or ethyl acetate in a sealed tube and irradiated for 3 h under the same conditions as in the photolysis of the diazoalkanes. The products were analysed by g.l.c. In most cases, the isomerization of the *syn*- and the *anti*-isomers to the *trans*-isomers was not observed or, if it occurred, was not significant (<6%). The only exception was the mixture of 1-(2-methyl-4-nitrophenyl)-*cis*-2,3-dimethylcyclopropane where 44% of the *syn*-isomer (1) was isomerized to the *trans*-isomer (3) under the given conditions.

[8/953 Received, 22nd May, 1978]

## REFERENCES

- <sup>1</sup> A. M. Trozzolo and E. Wasserman, 'Carbenes,' eds. R. A. Moss and M. Jones, Wiley, New York, 1975, vol. II, ch. 5,
- <sup>2</sup> C. D. Gutsche, G. L. Bachmann, and R. S. Coffey, *Tetrahedron*, 1962, **18**, 617.
- <sup>3</sup> G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, 1964, **86**, 4042.
- <sup>4</sup> G. L. Closs and S. H. Goh, *J.C.S. Perkin I*, 1972, 2103.
- <sup>5</sup> R. A. Moss and U. H. Dolling, *J. Amer. Chem. Soc.*, 1971, **93**, 954.
- <sup>6</sup> R. A. Moss and J. K. Huselton, *J. Amer. Chem. Soc.*, 1978, **100**, 1315.
- <sup>7</sup> S. H. Goh, *J.C.S. Chem. Comm.*, 1972, 512.
- <sup>8</sup> R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, 1969, **91**, 5681.
- <sup>9</sup> D. M. Doleib and Y. Iskander, *J. Chem. Soc. (B)*, 1967, 1154.
- <sup>10</sup> Suida, *Monatsh.*, 1912, **33**, 128.
- <sup>11</sup> W. F. Beech, *J. Chem. Soc. (C)*, 1967, 2374.
- <sup>12</sup> S. J. Angyal, *Org. Reactions*, 1954, **8**, 197.
- <sup>13</sup> L. Honner and E. H. Winkelmann, 'Newer Methods of Preparative Organic Chemistry,' ed. W. Foerst, Academic Press, New York, 1964, vol. III, p. 187.