

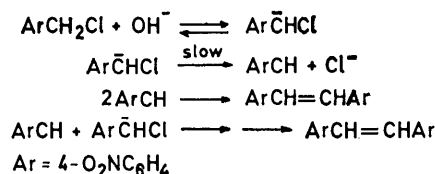
Nitrophenylcarbenes. Part II.^{1b} The Generation and Reactions of 4-Nitrophenylcarbene. Nature of the Reactions of 4-Nitrobenzyl Derivatives with Sodium Hydroxide

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4-Nitrophenylcarbene, generated by the catalytic and photolytic decomposition of α -dialzo-4-nitrotoluene, can be trapped by 2-butene. When produced photolytically the carbene adds non-stereospecifically to *cis*- and *trans*-but-2-enes to give a mixture of cyclopropane adducts, indicating a reaction of a triplet state. The reactions of sodium hydroxide with 4-nitrobenzyl chloride and dimethyl-4-nitrobenzylsulphonium ion were found to be sensitive to air. Reactions under nitrogen do not give 4,4'-dinitrostilbene as the sole product and bis-(4-nitrophenyl)-acetylene (10%) could also be isolated. α -Elimination in these reactions is unlikely and alternative mechanisms are discussed.

4-NITROBENZYL CHLORIDE on reaction with aqueous sodium hydroxide gives, instead of the expected 4-nitrobenzyl alcohol, 4,4'-dinitrostilbene.² The reaction has been known for a long time and appears to be a good method of preparing the *trans*-stilbene.³ Iskanda and Hanna⁴ studied the kinetics of the reaction and suggested an α -elimination mechanism (Scheme 1). Swain and



SCHEME 1

Thornton⁵ who studied the action of sodium hydroxide on dimethyl-4-nitrobenzylsulphonium ion also concluded that the mechanism of the reaction involved the

intermediacy of 4-nitrophenylcarbene. Although the mechanism is in agreement with the results reported several questions have remained unanswered. For instance, it is difficult to explain why the postulated carbene can neither add to olefins nor react with hydroxide ions which are present in high concentrations under the reaction conditions. Also, no satisfactory explanation has been provided as to why 4-nitrobenzyl chloride and the dimethylsulphonium ion could readily undergo α -elimination whereas other 4-nitrobenzyl derivatives, including the iodide,⁶ bromide,⁶ methylphenylsulphonium ion,⁷ pyridinium ion,⁸ and the trimethylammonium ion,⁸ cannot.

This paper describes the successful generation of 4-nitrophenylcarbene and a reinvestigation of the products from the reactions of 4-nitrobenzyl chloride and dimethyl-4-nitrobenzylsulphonium ion with sodium hydroxide.

Since the previous α -elimination methods^{4,7} did not

¹ (a) Taken in part from S. H. Goh, Ph.D. Thesis, University of Chicago, August 1968; (b) Part I, S. H. Goh, *J. Chem. Soc. (C)*, 1971, 2275.

² (a) C. A. Bischoff, *Ber.*, 1888, **21**, 2071; (b) G. Romeo, *Gazzetta*, 1905, **35**(1), 111; (c) K. Krassuski, *J. Russ. Phy. Chem. Soc.*, 1895, **27**, 339.

³ L. M. Litvinenko, I. F. Levchenko, and A. N. Androsov, *Zhur. obshchei Khim.*, 1958, **28**, 2046.

⁴ Y. Iskanda and S. B. Hanna, *J. Chem. Soc.*, 1961, 217.

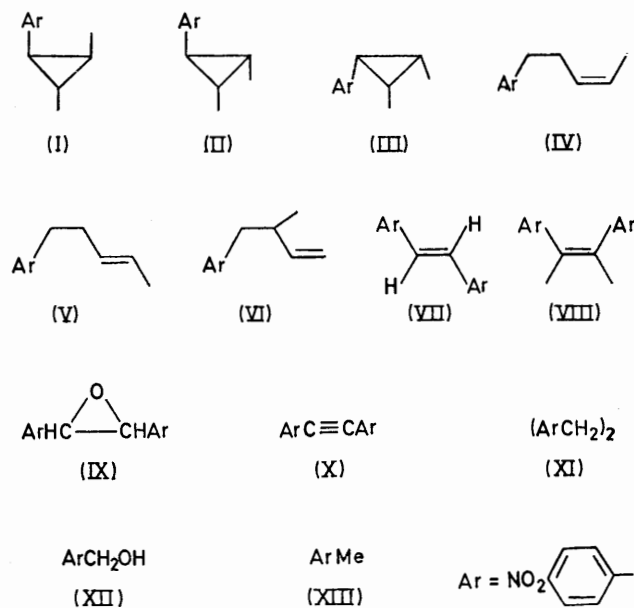
⁵ C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, 1961, **83**, 4033.

⁶ A. A. Abdullah, Y. Iskander, and Y. Riad, *J. Chem. Soc. (B)*, 1969, 1178.

⁷ I. Rothberg and E. R. Thornton, *J. Amer. Chem. Soc.*, 1964, **86**, 3296, 3302.

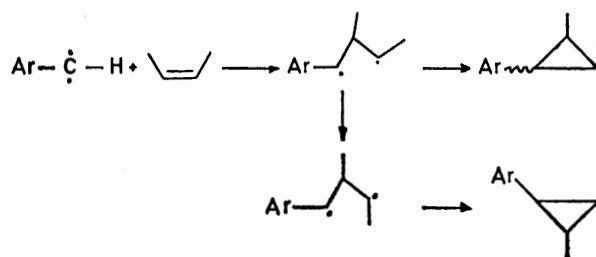
⁸ S. B. Hanna, *Chem. Comm.*, 1965, 487.

produce a 4-nitrophenylcarbene that could be identified by trapping with olefins, it was decided to generate the



carbene by another established method, namely from α -diazo-4-nitrotoluene. When the diazo-compound was decomposed catalytically or photolytically in the presence of but-2-ene moderate yields of cyclopropanes were obtained (Table 1). The photolytic reaction also

mechanism.¹⁰ The diradical intermediate formed may undergo bond rotation faster than spin inversion, thus destroying the stereochemical relationship originally present in the olefin (Scheme 2). This behaviour is somewhat in contrast to previously studied arylcarbenes;⁹ for example, phenylcarbene from phenyldiazomethane under the same conditions reacts with *cis*- and *trans*-but-2-enes to give non-stereospecific adducts amounting to not more than 3 and 1% respectively. This means that either the ring closure of the intermediate trimethylene diradical is slow or a fast spin relaxation occurs in 4-nitrophenylcarbene resulting in a large fraction of the addition by the triplet carbene. Another possibility which cannot be ruled out is that rapid singlet-triplet intersystem crossing occurs in the diazo-precursor;



SCHEME 2

this would not be surprising since the enhancement of such a process is known for nitro-compounds.¹¹

TABLE 1

Catalytic and photolytic reactions of α -diazo-4-nitrotoluene with but-2-ene

Reaction	Olefin	Yield *	Product distribution †					
			(I)	(II)	(III)	(IV)	(V)	(VI)
Photolysis	<i>trans</i> -But-2-ene	32	72.2	11.8	1.1	0.4	10.6	3.9
Photolysis	<i>cis</i> -But-2-ene	39	38.6	24.6	15.0	12.9	1.5	7.5
Catalysis ‡	<i>cis</i> -But-2-ene	31		21	79			

* Based on diazo-compound. † Yield (%) of total products. ‡ Copper ethyl acetoacetate catalyst.

gave olefinic insertion products in contrast to the catalytic process which gave only cyclopropane adducts. The structures of the products were established by their n.m.r. and mass spectra. The stereochemical identity of the isomeric cyclopropanes was found from their n.m.r. spectra; the *syn*-methyl protons being more shielded than the *anti*-methyl protons due to the anisotropy of the aromatic ring.^{1b,9} It may be noted that the addition of the free carbene (from photolysis) to but-2-ene is non-stereospecific. Non-stereospecificity of addition is usually taken as evidence for the involvement of a triplet carbene which adds to an olefin in a two-step

In the present instance it is not known whether the singlet-triplet interconversion occurs in the diazo-compound or in the carbene but the presence of a nitro-group in the *para*-position apparently stabilizes the triplet state. The triplet ground state of 4-nitrophenylcarbene is demonstrated by electron spin resonance in a glass at 77 K. Analysis of the spectrum yields a zero-field splitting, $D = 0.480 \text{ cm}^{-1}$, smaller than the value obtained for phenylcarbene ($D = 0.512 \text{ cm}^{-1}$)¹² indicating increased electron delocalization in the nitro-derivative.

The photolysis also give substantial amounts of olefinic

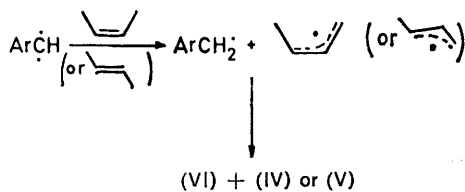
⁹ G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, 1964, **86**, 4042.

¹⁰ (a) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, 1956, **78**, 4496; (b) W. von E. Doering and P. LaFlamme, *ibid.*, p. 5447.

¹¹ (a) M. Kasha, *Radiation Res. Suppl.*, 1960, **2**, 243; (b) R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, 1969, **91**, 5681.

¹² (a) R. W. Brandon, G. L. Closs, and C. A. Hutchinson, jun., *J. Chem. Phys.*, 1962, **37**, 1878; (b) A. M. Trozzolo, E. Wasserman, and R. W. Murray, *J. Amer. Chem. Soc.*, 1962, **84**, 4990.

insertion products in contrast to the behaviour of other arylcarbenes¹⁰ where such products are obtained in negligible quantities. Insertion to allylic carbon-hydrogen bonds is also typical of triplet carbenes and the two-step abstraction-recombination mechanism is shown in Scheme 3. Such reactions resemble those of diphenylcarbene and fluorenylidene.¹³



SCHEME 3

The present results show that free 4-nitrophenylcarbene as well as the copper carbenoid species can be readily trapped by olefins. The failure of previous attempts^{4,7} to obtain cyclopropane adducts from α -eliminations of 4-nitrobenzyl chloride or dimethyl-4-nitrobenzylsulphonium toluene-*p*-sulphonate means that the intermediacy of the same carbene is unlikely in these reactions. Previously it was assumed⁷ that 4-nitrophenylcarbene was extremely selective in its reactions so that

nitrostilbene as reported.⁴ Column chromatography of the crude material through Florisil and examination of the eluted fractions by n.m.r. spectroscopy and t.l.c. showed that the total yield of 4,4'-dinitrostilbene amounted to not more than 66% in contrast to the 100% reported. Of interest is the minor product bis-(4-nitrophenyl)acetylene isolated in *ca.* 10% yield. This was not detected by previous workers but the m.p. 212° corresponds to a product (m.p. 210–216°) isolated by Walden and Kernbaum.¹⁴ This, in all probability, was the compound erroneously assigned as *cis*-4,4'-dinitrostilbene (m.p. 183–185°); the elemental analysis reported corresponds, in fact, much more to the alkyne than to the alkene.

Other minor products detected from reactions conducted in the absence of air include 4,4'-dinitrobenzyl, 4-nitrobenzyl alcohol, and 4-nitrotoluene (Table 2). A small quantity of material which was eluted rather slowly, however, remained unidentified. This is probably a complex mixture of products from oxidation-reduction involving the nitro-group; complex products are known to be formed from nitroaromatics in basic solution *via* radical-anions.^{8,15,16}

The decomposition of dimethyl-4-nitrobenzylsulphonium ion in aqueous sodium hydroxide was also studied under various conditions and the products obtained are

TABLE 2

Reaction of 4-nitrobenzyl chloride with sodium hydroxide

No.	Reaction conditions			Product yield *						
	[ArCH ₂ Cl] ^b	[NaOH] ^b	Temp. (°C)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)
(i)	0.2	0.3	40 (N ₂) ^c	61	5	0	10	2	0.4 ^d	0.5
(ii)	0.05	0.375	25 (N ₂)	61	2	0	9	2		
(iii)	0.01	0.14	24 (N ₂)	62	2	0	8		1	0.6
(iv)	0.01	0.1	23 (Air)			33 (65) ^e				
(v)	0.05	0.05	30 (Air)	51		18 (19) ^e				

* Yield (%) based on 4-nitrobenzyl chloride. ^b Initial concentration in mol l⁻¹. Reaction (i) was run in 90% ethanol, the rest in 50% dioxan-water. ^c N₂ or air indicate that the reaction was carried out under nitrogen or in the presence of air. ^d Also isolated, ethyl 4-nitrobenzyl ether (2%). ^e Number in parentheses gives the yield of *cis*-4,4'-dinitrostilbene oxide.

olefins and hydroxide ions cannot compete with other carbanions (*e.g.* α -chloro-4-nitrobenzyl carbanion) for the carbene.

In view of the above results it was found necessary to reinvestigate the previously reported α -eliminations. The reaction of 4-nitrobenzyl chloride with sodium hydroxide was carried out under various conditions and the results are summarised in Table 2. The reaction was very sensitive to traces of air or oxygen. In the presence of air the major products were *cis*- and *trans*-4,4'-dinitrostilbene oxide but when the reaction was carried out under nitrogen the main product was 4,4'-dinitrostilbene. An examination of the crude product of the latter reaction revealed that it was not pure 4,4'-di-

summarized in Table 3. Contrary to previous reports^{5,7} 4,4'-dinitrostilbene was not the sole product but only the major product in up to 74% yield. By column chromatography through alumina or Florisil about 10% *trans*-4,4'-dinitrostilbene oxide could also be isolated. Other minor products detected include 4-nitrobenzyl alcohol, 4-nitrotoluene, and 4,4'-dinitrobenzyl. Some material which was eluted rather slowly remained unidentified; this is likely to be a complex mixture of oxidation-reduction products involving the nitro-group. The formation of these side products is not too surprising since in related work on other nitrobenzylsulphonium derivatives⁷ as high as 50–72% of such unidentifiable products have been encountered.

¹³ (a) W. von E. Doering and M. Jones, jun., *Tetrahedron Letters*, 1963, 791; (b) E. Funakubo, I. Moritani, T. Nagai, S. Nishida, and S. Murahashi, *ibid.*, p. 1069; (c) M. Jones, jun., and K. R. Rettig, *J. Amer. Chem. Soc.*, 1965, **87**, 4013, 4015.

¹⁴ P. Walden and A. Kernbaum, *Ber.*, 1890, **22**, 1958.

¹⁵ (a) N. Kornblum and P. Pink, *Tetrahedron*, 1963, **19**, 17; (b) N. Kornblum, R. C. Kerber, and G. W. Urry, *J. Amer. Chem. Soc.*, 1965, **87**, 4520.

¹⁶ G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, 1962, **84**, 4153.

The formation of *trans*-4,4'-dinitrostilbene oxide was not due to inadvertent traces of air since careful deoxygenation of the reaction vessels did not result in its elimination. Epoxide formation is, however, not un-

series of 4-nitrobenzyl compounds. For a number of typical compounds represented in Scheme 4 it may be seen that the nature of the major product formed appears to be dependent on the 'ease of displacement'

TABLE 3

Reaction of dimethyl-4-nitrobenzylsulphonium ion with sodium hydroxide

Reaction conditions				Product yield ^a					
No.	[ArCH ₂ ⁺ SMe ₂] ^b	[NaOH] ^b	Temp. (°C)	(VII)	(VIII)	(IX) ^d	(XII)	(XI)	(XIII)
(i)	0.1	0.2	90 (N ₂) ^c	72	2	9	0.3	1	1
(ii)	0.1	0.1	55 (N ₂)	68		9			
(iii)	0.01	0.02	60 (N ₂)	67	3	18	3		0.6
(iv)	0.1	0.1	55 (Air)	69		27			
(v)	0.02	0.04	60 (Air)	32		60	1.2		
(vi)	0.01	0.4	24 (O ₂)			85			

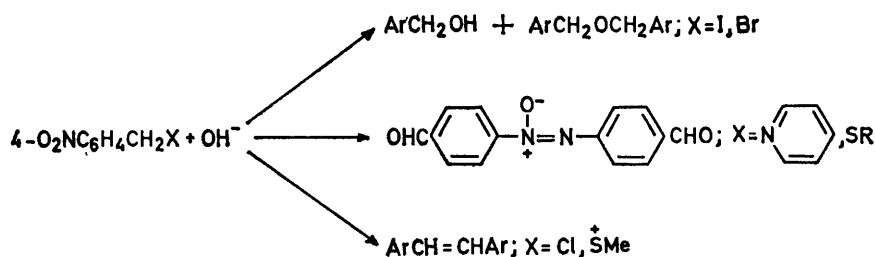
^a Yield (%) based on the sulphonium ion. ^b Initial concentration in mol l⁻¹. ^c N₂, air, or O₂ indicate that the reaction was carried out under an atmosphere of nitrogen, air, or oxygen respectively. ^d *trans*-Isomer.

usual since it is known that dimethyl-3-nitrobenzylsulphonium bromide reacts with sodium hydroxide under nitrogen to give 41% of *trans*-3,3'-dinitrostilbene oxide. Recently, Iskanda and Doleib¹⁷ also reported the formation of epoxides from a similar reaction of 3-methyl-4-nitrobenzyl chloride. 4,4'-Dinitrostilbene oxide probably arises from intermediate 4-nitrobenzaldehyde which is known to react rapidly with nitrobenzyl carbanion to give the epoxide. 4-Nitrobenzaldehyde may be produced in an analogous manner as the 'oxygen alkylation product' reported by Kornblum¹⁵ from the reaction of nitroparaffin salts with 4-nitrobenzyl chloride.

The low yield of 4-nitrobenzyl alcohol obtained from the present study (Table 3) is rather surprising, even when low concentrations of the sulphonium ion were

or 'departing ability' of the leaving groups in the order I > Br > Cl ~ SMe₂ > pyridine > SR.¹⁸ With good leaving groups ordinary S_N2 displacement by hydroxide ion occurs while with poorer leaving groups such as chloride and dimethylsulphonium, stilbene formation becomes predominant. With still poorer leaving groups such as pyridine and sulphide, the major product becomes the azoxy-compound.

In view of the new evidence presented, it is necessary to formulate a non-carbene mechanism for the reaction of 4-nitrobenzyl chloride or dimethyl-4-nitrobenzylsulphonium ion with sodium hydroxide. This is given in Scheme 5 and involves electron transfer from carbanions to neutral molecules resulting in the formation of



SCHEME 4

used. However, it was found that added 4-nitrobenzyl alcohol has the effect of increasing the yield of 4,4'-dinitrostilbene oxide. Apparently, the alcohol is able to function as a nucleophile and the formation of the stilbene oxide may, in part, be due to the alcohol formed as a side product.

It is instructive to compare the dependence of the products formed on the nature of the leaving group for a

radicals and radical-ions as short-lived intermediates. This electron transfer step is a well documented process and is, in fact, the key step in several reactions of 4-nitrobenzyl derivatives in basic media.¹⁵ The lifetimes of the radical anions of 4-nitrobenzyl chloride and the sulphonium ion are known to be short because they decompose rapidly to 4-nitrobenzyl radicals.^{19,20} The mechanism explains the formation of bis-(4-nitrophenyl)-acetylene as a side-product *via* dimerisation of the radical

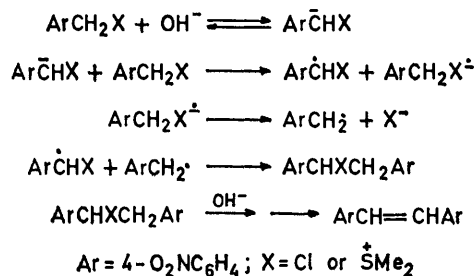
¹⁷ Y. Iskander and D. M. Doleib, *J. Chem. Soc. (B)*, 1967, 1154, 1159.

¹⁸ (a) J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962, p. 184; (b) E. M. Kosower, 'An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968, p. 81.

¹⁹ G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, 1968, **90**, 347.

²⁰ M. Mohammad, J. Hajdu, and E. M. Kosower, *J. Amer. Chem. Soc.*, 1971, **93**, 1792.

$\text{Ar}\dot{\text{C}}\text{HCl}$; in the case of the reaction of the sulphonium ion the radical $\text{Ar}\dot{\text{C}}\text{HSMe}_2$ apparently fails to dimerise because of polar effects, but if radical coupling occurs at the oxygen atom of the nitro-group, the result would be an 'oxygen alkylation product' or 4-nitrobenzaldehyde¹⁵ which will subsequently yield 4,4'-dinitrosilbene oxide.



SCHEME 5

The mechanism is also in accord with new kinetic results obtained from experiments conducted with the careful exclusion of air;²¹ under this condition the reaction is first order in hydroxide ion and second order in the nitro-compound. A competing $\text{S}_{\text{N}}2$ reaction of the carbanion and the reactant to give dinitrostilbene is however not excluded. Such a mechanism is in fact favoured by Shipp²² for the reaction of trinitrobenzyl chloride with sodium hydroxide.

EXPERIMENTAL

M.p.s were uncorrected. N.m.r. spectra were recorded with Varian A60A and A56-60 instruments; chemical shifts are reported as δ (p.p.m.) downfield from tetramethylsilane as internal standard. G.l.c. was performed with an Aerograph A90P instrument; columns used were made from $\frac{1}{8}$ or $\frac{1}{4}$ in copper tubing with HMDS Chromosorb W as solid support. T.l.c. was performed using Eastman alumina or silica gel chromatogram sheets. Mass spectra were obtained from an AEI model MS-9 double-focusing spectrometer.

α -Diazo-4-nitrotoluene.—4-Nitrobenzaldehyde hydrazone²³ was oxidized by mercuric oxide in ethyl acetate-carbon tetrachloride to give α -diazo-4-nitrotoluene (52%).

Photolysis of α -Diazo-4-nitrotoluene in *cis*-But-2-ene.—The diazo-compound (5 mmol) was dissolved in 100 ml of 60% *cis*-but-2-ene in ethyl acetate. The solution was photolysed by a 300 W sun-lamp through Pyrex glass for 10 h at 15–20°, with gentle stirring. The solvents were then removed by evaporation under reduced pressure and n.m.r. spectroscopy showed that yield of products was 39% with ca. 37% of diazo-compound unchanged. Column chromatography of the crude material through alumina using pentane as eluant gave the desired hydrocarbon products. By g.l.c. with a 9 ft \times $\frac{1}{4}$ in SE-30 column the following hydrocarbons were isolated, listed according to the order of elution from the column. 3-Methyl-4-(*p*-nitrophenyl)but-1-ene (7.5%) had δ (CCl_4) 1.02 (3H, d, J 6.5 Hz, >CHMe),

2.4–2.7 (3H, m, allylic and benzylic H), 4.7–5.05 (2H, m, = CH_2), 5.4–6.0 (1H, m, $-\text{CH}=\text{}$), 7.22 (2H, d, J 9 Hz, aromatic), and 8.07 (2H, d, J 9 Hz, aromatic) [Found: M^+ , 191.09433 (mass spectrum). $\text{C}_{11}\text{H}_{13}\text{NO}_2$ requires M , 191.09462]. 1,trans-2-Dimethyl-cis-3-(*p*-nitrophenyl)cyclopropane (33.6%) had δ (CCl_4) 0.88br (3H, s, *syn*-Me), 1.22br (5H, s, *anti*-Me and cyclopropyl H), 1.83 (1H, t, J 6 Hz, ArCH), 7.23 (2H, d, J 8.5 Hz, aromatic), and 8.08 (2H, d, J 8.5 Hz, aromatic) [Found: M^+ , 191.09433 (mass spectrum)].

5-(*p*-Nitrophenyl)-trans-pent-2-ene (1.5%) was identified by its retention times on 5 ft \times $\frac{1}{8}$ in CW-20M and 9 ft \times $\frac{1}{4}$ in SE-30 g.l.c. columns. An authentic sample is described below. 5-(*p*-Nitrophenyl)-cis-pent-2-ene (12.9%) had δ (CCl_4) 1.53 (3H, d, J 5 Hz, = CHMe), 2.25–2.55 (2H, m, allylic and benzylic H), 5.2–5.55 (2H, m, olefinic), 7.29 (2H, d, J 8.5 Hz, aromatic), and 8.10 (2H, d, J 8.5 Hz, aromatic) [Found: M^+ , 191.09433 (mass spectrum)]. 1,cis-2-Dimethyl-trans-3-(*p*-nitrophenyl)cyclopropane (24.6%) had δ (CCl_4) 1.23br (9H, s, cyclopropyl and Me), 7.01 (2H, d, J 8.5 Hz, aromatic), and 8.0 (2H, d, J 8.5 Hz, aromatic) [Found: M^+ , 191.09350 (mass spectrum)]. 1,cis-2-Dimethyl-cis-3-(*p*-nitrophenyl)cyclopropane (15%) had δ (CCl_4) 0.95 (6H, d, J 5 Hz, $2 \times \text{>CHMe}$), 1.0–1.5 (2H, m, cyclopropyl H), 2.04 (1H, t, J 8 Hz, ArCH), 7.3 (2H, d, J 8.5 Hz, aromatic), and 8.07 (2H, d, J 8.5 Hz, aromatic) [Found: M^+ , 191.09768 (mass spectrum)].

Photolysis of 4-Nitrophenyldiazomethane in *trans*-But-2-ene.—Photolysis was carried out in a similar way and the yield of products based on reacted diazo-compound was 32%. The products were identified by g.l.c. on a 5 ft CW-20M and a 9 ft SE-30 column. Using the latter column the products were eluted in the order 3-methyl-4-(*p*-nitrophenyl)but-1-ene (3.9%), 1,trans-2-dimethyl-3-(*p*-nitrophenyl)cyclopropane (72.2%), 5-(*p*-nitrophenyl)-trans-pent-2-ene (10.6%), 5-(*p*-nitrophenyl)-cis-pent-2-ene (0.4%), 1,cis-2-dimethyl-trans-3-(*p*-nitrophenyl)cyclopropane (11.8%), and 1,cis-2-dimethyl-cis-3-(*p*-nitrophenyl)cyclopropane (1.1%). 5-(*p*-Nitrophenyl)-trans-pent-2-ene had δ (CCl_4) 1.57–1.7 (3H, m, = CHMe), 2.2–2.5 (2H, m, allylic H), 2.6–2.9 (2H, m, Ar CH_2), 5.3–5.5 (2H, m, olefinic), 7.26 (2H, d, J 8.5 Hz, aromatic), and 8.11 (2H, d, J 8.5 Hz, aromatic), ν_{max} 970 cm^{-1} [Found: M^+ , 191.09433 (mass spectrum)].

Catalytic Decomposition of α -Diazo-4-nitrotoluene in *cis*-But-2-ene.— α -Diazo-4-nitrotoluene (3.3 mmol) in carbon tetrachloride (25 ml) was added slowly over 3 h to a stirred solution of dry copper ethyl acetoacetate (0.1 g) in *cis*-but-2-ene (10 ml) and carbon tetrachloride (10 ml). After distilling off the solvents, the products were extracted with pentane (5 \times 15 ml). N.m.r. spectroscopy and g.l.c. analysis showed a 31% yield of cyclopropane adducts, the *syn*:*anti* isomer ratio being 3.7. These cyclopropanes do not isomerise under the conditions of previous photolytic experiments.

Triplet Spectrum of 4-Nitrophenylcarbene.—A 0.05M solution of α -diazo-4-nitrotoluene in ethyl acetate-isopentane was photolysed at 77 K in the cavity of a Varian 4500 e.s.r. spectrometer. The zero-field parameters²⁴ found for the triplet carbene were $D = 0.480$ and $E = 0.0214 \text{ cm}^{-1}$.

Reactions of 4-Nitrobenzyl Chloride and Dimethyl-4-nitrobenzylsulphonium ion with Sodium Hydroxide.—General.

²³ T. Curtis and A. Lublin, *Ber.*, 1900, **33**, 2460.

²¹ G. L. Closs and S. H. Goh, *J.C.S. Perkin II*, 1972, 1473.

²² (a) K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, 1966, **31**, 857; (b) K. G. Shipp, *ibid.*, 1964, **29**, 2620.

²⁴ (a) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 1964, **41**, 1769; (b) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, 1965, **87**, 129.

4-Nitrobenzyl chloride and dimethyl-4-nitrobenzylsulphonium toluene-*p*-sulphonate, bromide, or perchlorate were prepared as reported.⁴⁻⁷ Linde nitrogen gas was used after passing it through chromous solution. Reactions of the nitrobenzyl compounds were carried out under various conditions and the products were collected by filtration after distilling off the organic solvents. The crude products were examined by n.m.r. spectroscopy in hot solutions (*ca.* 50°) of [²H₆]dimethyl sulphoxide or deuteriochloroform; volatile compounds were subjected to g.l.c. analysis. In every reaction the products were chromatographed through Florisil or alumina and the eluted fractions were qualitatively analysed by n.m.r. spectroscopy and t.l.c. Quantitative estimates were made by weighing the fractions after removal of the solvent in conjunction with n.m.r. spectra. In deuteriochloroform the benzylic protons of 4-nitrotoluene, 4-nitrobenzyl chloride, 4-nitrobenzyl alcohol, 4-nitrobenzyl ether, and 4,4'-dinitrobenzyl, have n.m.r. absorptions at δ 2.48, 4.64, 4.83, 4.73, and 3.07 p.p.m. respectively. In the same solvent *cis*- and *trans*-4,4'-dinitrostilbene oxides have characteristic absorptions at δ 4.52 and 3.99 p.p.m. respectively while the α, α' -protons of *cis*-4,4'-dinitrostilbene²⁵ absorb at δ 6.83 p.p.m. In [²H₆]dimethylsulphoxide *cis*- and *trans*-4,4'-dinitrostilbenes have absorptions at δ 7.00 and 7.52 p.p.m. respectively for the α, α' -protons while the corresponding epoxides have characteristic absorptions at δ 4.75 and 4.40 p.p.m. respectively.

Reaction of 4-nitrobenzyl chloride with sodium hydroxide. A typical experiment was conducted as follows. 4-Nitrobenzyl chloride (0.856 g) was dissolved in deoxygenated dioxan (50 ml) and deoxygenated water (30 ml). Deoxygenated 2M-sodium hydroxide solution (15 ml) was added and the mixture was shaken and left for 24 h under nitrogen. The yellow suspension was made just acid by adding dilute hydrochloric acid and the yellow solids were filtered in a sintered glass funnel and washed with water. A small crop of solid could further be obtained by concentration of the filtrate. After drying to constant weight (0.688 g), portions of this were chromatographed through Florisil and alumina and eluted successively with benzene, methylene chloride, chloroform, and methanol. The eluted fractions were evaporated, dried, weighed, and then ana-

lysed by t.l.c. and n.m.r. spectroscopy. Eluted first was bis-(4-nitrophenyl)acetylene as light straw crystals, m.p. 212° (lit.,²⁶ 210–212°), δ (CDCl₃) 7.67 (4H, d, *J* 9 Hz) and 8.24 (4H, d, *J* 9 Hz) [Found: *M*⁺, 268 (mass spectrum). Calc. for C₁₄H₈N₂O₄⁺: *M*, 268]. The major product, *trans*-4,4'-dinitrostilbene, was eluted next. Later fractions show ill-defined peaks in the n.m.r. spectra and could not be identified. The results of other experiments under various conditions are given in Table 2.

Reaction of dimethyl-4-nitrobenzylsulphonium ion with sodium hydroxide. A typical experiment was carried out as follows. The sulphonium bromide (2.77 g) was dissolved in deoxygenated water (100 ml). Deoxygenated 2M-sodium hydroxide solution (10 ml) was syringed in and the mixture was heated at 90° for 1½ h. After cooling the solution was acidified by concentrated hydrochloric acid and the yellow solids filtered and dried (1.33 g). Traces of 4-nitrotoluene, 4-nitrobenzaldehyde, and 4-nitrobenzyl alcohol could be obtained by ether extraction of the filtrate.

A fraction of the crude product (0.571 g) dissolved in chloroform was chromatographed through Florisil, eluting successively with benzene, methylene chloride, and methanol. First eluted was a trace of 4-nitrotoluene and followed by *trans*-4,4'-dinitrostilbene oxide (9%). Crystalline *trans*-4,4'-dinitrostilbene was obtained as a major product but minor amounts of the *cis*-isomer could be detected from the n.m.r. spectra. Later fractions had ill-defined n.m.r. spectra and could not be identified. Product distributions for reactions carried out under various conditions are given in Table 3. The dinitrostilbenes were stable under reaction conditions. When olefins were added to this reaction and that of 4-nitrobenzyl chloride, cyclopropanes were not formed.

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