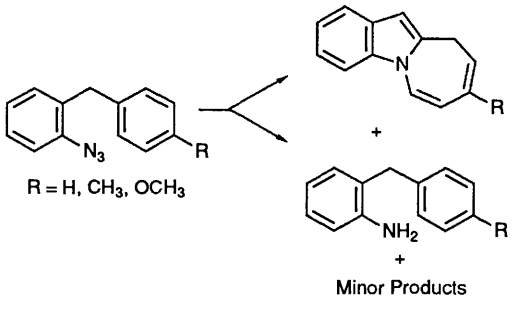
Intramolecular Nitrene Insertions into Aromatic and Heteroaromatic Rings. Part 9.[1] Synthesis of 2-Azidodiphenylmethanes and the Kinetics of their Thermal Decomposition in Solution

Gurnos Jones,* Brian D. Long and Melanie P. Thorne
Department of Chemistry, University of Keele, Keele, Staffordshire ST5 5BG, UK

The synthesis of some new *o*-azidodiphenylmethanes **3b**, **10**, **15**, **18**, **21** and **22** is described. The first-order kinetics of the thermal decomposition in trichlorobenzene of these and some previously studied azides (**3a**, **3c** and **3d**) has been studied in the range 140–180 K. The initial step is evolution of nitrogen and formation of a nitrene intermediate, which reacts to give a 10*H*-azepinoindole together with some amine. Rate constants for the first step were compared with those for product formation and show it to be the rate-determining factor. Electron-donating substituents *para* to the azide group stabilise the incipient nitrene by resonance interactions (rate constants correlate with σ_R·) yielding higher proportions of amine products, which result from the spin forbidden singlet–triplet nitrene transition. Substituents at the 4′-position influence the nature of the products but not decomposition rates. A new compound, 1a-methoxy-1a,9b-dihydro-1*H*-cyclopropa[1′,2′:3,4]pyridol[1,2-*a*]indole (**28**), is obtained from 2-azido-4′-methoxydiphenylmethane (**3d**) in addition to the expected azepinoindole and amine. Kinetic measurements show that it is an intermediate in one, but not the sole, route to formation of 8-methoxyazepinoindole **27** from **3d**.

We have published a number of papers on the thermal decomposition of *o*-azidodiphenylmethanes[2–5] but we have not previously used kinetic methods. In this paper we record the synthesis of a number of new 2-azidodiphenylmethanes and the effect of substituents on the rates and products of the thermal decomposition in trichlorobenzene of a series of 4′- and 5-substituted 2-azidodiphenylmethanes.

The initial step in azide decompositions is usually nitrogen loss with formation of a nitrene intermediate, which rapidly undergoes further reaction. The type and number of the products depends on the substituents, solvent and reaction conditions. Thus 2-azidodiphenylmethane and its 4′-methyl and 4′-methoxy derivatives have been shown to yield ring-expanded azepinoindoles together with amines and smaller quantities of acridines and acridans[5–7] (Scheme 1).



Scheme 1

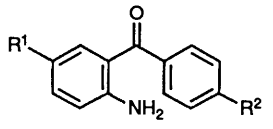
The intermediacy of the nitrene species in azide decompositions has usually been assumed from consideration of the nature of the products, but direct evidence for its participation in some reactions, *e.g.* the decomposition of 2-azidobiphenyls has been found both from kinetic studies of thermolysis reactions[8] and spectroscopically from photochemical decompositions.[9] Spin conservation dictates that the nitrene generated in the thermal process is in the singlet state. Transition to the triplet state by inter-system-crossing, being spin forbidden, is slow relative to the lifetime of the nitrene, but it has been found to occur in some azide decompositions.[10] Reaction pathways involving both singlet and triplet nitrene have been proposed.[11]

Very few kinetic studies of azide decompositions have been undertaken. Smith and Hall[8] have shown that substituents on the azide-bearing ring have only a minor effect on the rates of nitrogen release from 2-azidobiphenyls, rates and product types being unaffected by substituents on the second ring. Dyall[12] and Smith[8] have shown that in phenyl azide decompositions all substituents *para* to the azide group produce a small rate increase, and likewise with *ortho* substituents,[12] except where α,β unsaturation in the substituent enables it to become specifically involved in the transition state.

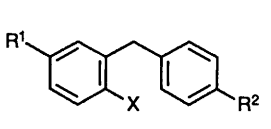
We have now studied the thermal decompositions in trichlorobenzene of the seven 2-azidodiarylmethanes, **3a–d**, **10**, **15** and **18**. The change in azide concentration with time has been monitored by measurement of the *rate* of nitrogen evolution using a GLC technique developed in these laboratories for studying first-order reactions which yield gaseous products.[13] Rates of product formation for compounds **3c** and **3d** have also been investigated as well as the changing pattern of product ratios as decomposition temperatures are altered.

Syntheses.—Of the azides **3a–d**, **10**, **15** and **18** used in the kinetic work three (**3a**, **c**, **d**), have previously been reported. Using our standard synthetic route,[2] reduction of the aminobenzophenones **1a–d** by sodium in ethanol gave aminodiphenylmethanes **2a–d**, which were converted by diazotisation and treatment with sodium azide into the azides **3a–d**. The aminobenzophenones were prepared from acetanthranil or a 6-substituted acetanthranil,[14] the only benzophenone prepared for the first time by this route being **1b**. This compound had previously been obtained in 5% yield by a rearrangement reaction;[15,16] in our route it was also the minor product (15%), the major product being the triphenylmethanol **4**.

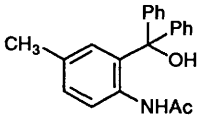
Our standard route was unsuitable for the two nitro-substituted azides required and other approaches were examined. Nitration of 3-methoxydiphenylmethane (**5**) gave a mixture of three nitro(methoxy)diphenylmethanes in isolated yields of 49% (**A**), 23% (**B**) and 12% (**C**) (Scheme 2). Chromatography gave a pure sample of the major product **A**; recrystallisation of



1a; $R^1 = R^2 = H$
1b; $R^1 = Me$, $R^2 = H$
1c; $R^1 = H$, $R^2 = Me$
1d; $R^1 = H$, $R^2 = OMe$

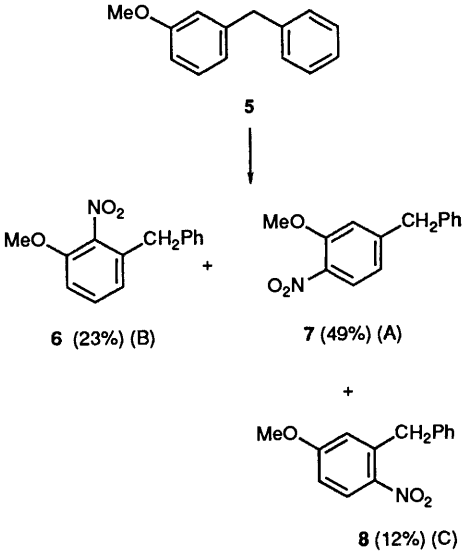


2a; $R^1 = R^2 = H$, $X = NH_2$
2b; $R^1 = Me$, $R^2 = H$, $X = NH_2$
2c; $R^1 = H$, $R^2 = Me$, $X = NH_2$
2d; $R^1 = H$, $R^2 = OMe$, $X = NH_2$
3a; $R^1 = R^2 = H$, $X = N_3$
3b; $R^1 = Me$, $R^2 = H$, $X = N_3$
3c; $R^1 = H$, $R^2 = Me$, $X = N_3$
3d; $R^1 = H$, $R^2 = OMe$, $X = N_3$
9; $R^1 = OMe$, $R^2 = H$, $X = NH_2$
10; $R^1 = OMe$, $R^2 = H$, $X = N_3$
14; $R^1 = H$, $R^2 = NO_2$, $X = NH_2$
15; $R^1 = H$, $R^2 = NO_2$, $X = N_3$
17; $R^1 = R^2 = NO_2$, $X = NH_2$
18; $R^1 = R^2 = NO_2$, $X = N_3$



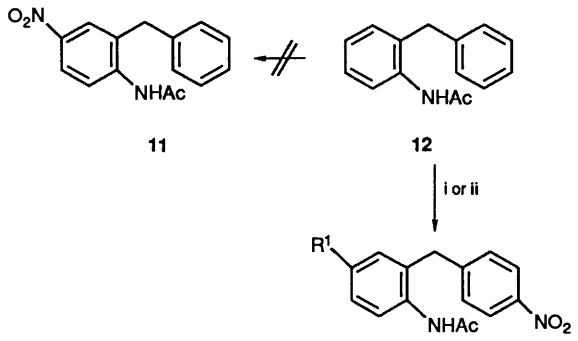
4

the unresolved pair of minor components gave compound **B** and further chromatography gave compound **C**. All three were nitrated on the methoxylated ring, as expected, and the absence of an upfield NMR singlet (or slightly split doublet) in compound **B** established this as the 3-methoxy-2-nitrodiphenylmethane **6**. The structures of isomers **A** and **C** were established by ^{13}C NMR spectroscopy, the chemical shifts for compound **A** matching those calculated for 3-methoxy-4-nitrodiphenylmethane (**7**), and those of compound **C** matching the calculated values for 3-methoxy-6-nitrodiphenylmethane (**8**), the required compound. The structure of **8** was further confirmed by its conversion into the amine **9** and azide **10** which underwent the usual insertion reactions as described below.



Scheme 2

Our final aim was to prepare 2-azido-5-nitrodiphenylmethane and, if possible, 2-azido-4′-nitrodiphenylmethane (**15**). A preparation of the amide **11** had been reported[17] by nitration of 2-acetamidodiphenylmethane (**12**), using a mixture of nitric and sulfuric acids with acetic anhydride, with subsequent deacetylation (Scheme 3). We followed the experimental instructions of Davies *et al.*[17] and obtained a compound of similar m.p. to that described. The ^1H NMR spectrum showed a clean AA′BB′ pattern of signals at δ 7.2 and 8.0 which can only be explained by nitration in the unsubstituted ring to give the isomer **13**. We are grateful to Dr. R. B. Moodie for drawing our attention to his paper describing the relative rates of nitration of *p*-toluidine and benzene, the latter being the faster.[18] Hydrolysis of amide **13** gave the amine **14**, which had the same m.p. as the amine reported by Davies *et al.*;[17] the ^1H NMR spectrum again confirmed substitution in the second ring. Normal conversion of amine into azide gave compound **15**. More vigorous nitration of compound **12** (mixed acid at 60 °C) gave a dinitro derivative, confirmed by NMR spectroscopy as 2-acetamido-4′,5-dinitrodiphenylmethane (**16**). Deacetylation gave the amine **17** and hence the azide **18**. The monosubstituted 2-azido-5-nitrodiphenyl methane could not be obtained.

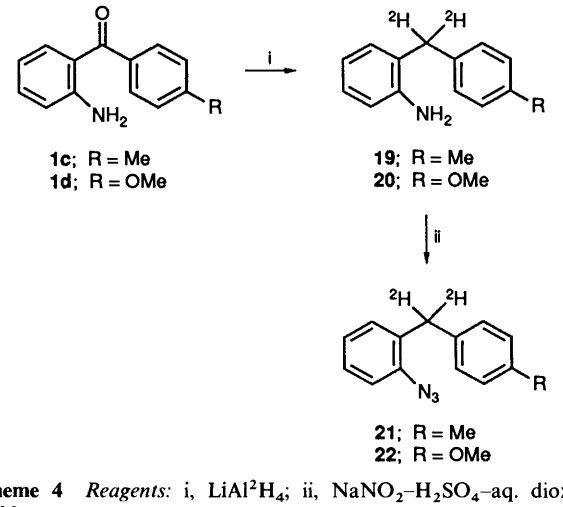


11 **12**

13; $R^1 = H$
16; $R^1 = NO_2$

Scheme 3 *Reagents:* i, HNO_3–H_2SO_4–Ac_2O, −5 °C; ii, H_2SO_4–HNO_3, 60 °C

Two azidodideuteriodiphenylmethanes (**21** and **22**) were prepared for mechanism studies, by reduction of aminobenzophenones **1c** and **1d** using lithium aluminium deuteride and aluminium chloride to give the amines **19** and **20**, with subsequent diazotization and reaction with sodium azide (Scheme 4). Neither showed a signal in the region δ 3.5–3.8 characteristic of the methylene group in diphenylmethanes.



1c; R = Me
1d; R = OMe

19; R = Me
20; R = OMe

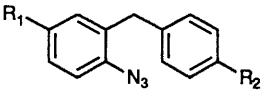
21; R = Me
22; R = OMe

Scheme 4 *Reagents:* i, $LiAl^2H_4$; ii, $NaNO_2$–H_2SO_4–aq. dioxane–NaN_3

Results

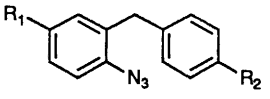
Rate Constants from Nitrogen-release Measurements.—The azides were decomposed in 1,2,4-trichlorobenzene, in a vessel through which helium was passed at a carefully controlled rate of about 15 cm^3 min^{-1}. The nitrogen evolved from the reaction was swept in the helium flow into a 10 cm^3 gas-sampling loop, attached to the gas chromatograph. Automatic GLC sampling of the gas in the loop at regular intervals, usually of 6 min, gave a measure of the concentration of nitrogen in the helium flow and therefore of the *rate* of nitrogen release from the reactant.

Table 1 Rate constants ($k/10^{-4}$ s^{-1}) for the thermal decomposition of 2-azidodiarylmethanes



			T/°C										
Compound	R^1	R^2	145.3	150.0	155.0	160.0	163.0	168.0	170.0	173.0	180.0	182.0	185.0
1	H	H					3.74	5.51		8.42			19.8
3c	H	CH_3					3.57	5.51	6.27	8.31	12.39		19.65
3d	H	OCH_3					3.88	5.99		8.77			20.81
15	H	NO_2				2.86			5.86		13.01		18.31
3b	CH_3	H		1.86		4.65			8.74			19.63	
10	OCH_3	H	7.37	10.77		19.06			39.5				
18	NO_2	NO_2		0.82	1.28	2.12			5.46		13.06		16.87

Table 2 Activation parameters for the decomposition of 2-azidodiarylmethanes



R^1	R^2	E_a/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
H	H	124.8 ± 5.6	121.2 ± 5.5	−35.3 ± 12.3
H	CH_3	123.4 ± 10.8	119.7 ± 10.6	−39.4 ± 23.6
H	OCH_3	125.0 ± 7.9	121.3 ± 7.7	−35.5 ± 17.4
H	NO_2	125.1 ± 9.2	121.4 ± 8.7	−35.9 ± 16.0
CH_3	H	116.2 ± 9.5	112.6 ± 9.2	−52.7 ± 21.0
OCH_3	H	100.5 ± 8.9	96.9 ± 8.7	−75.9 ± 20.3
NO_2	NO_2	140.3 ± 17.0	136.6 ± 15.3	4.9 ± 4.5

For a first-order reaction, the rate of gas release is proportional to the concentration of reactant,[13] hence the rate constants can be determined from plots of log (peak area) against time. Good straight lines were obtained in all cases. Reactions were usually followed for at least three half-lives and the rate constants, k, obtained by linear least-squares analysis of the plots ($R > 0.99$). Duplicate values agreed to within ± 5%. The results are given in Table 1 and show that only substituents on the same ring as the azide group (at R^1) have any appreciable effect on the reaction rates, electron-donating groups being rate enhancing and *vice versa*.

The activation parameters (Table 2) were determined over a temperature range of not less than 22 °C. Studies over a larger temperature range could not be done using this analytical technique.

Decomposition Products.—Attempts have been made to study the variation in yield of the different decomposition products using a combination of gas chromatography, HPLC, and ^{1}H NMR spectroscopy. In our previous papers[2–5,19] we were interested only in major products and decompositions were done over a narrower range of temperatures. The new experiments have shown the presence of a number of previously undiscovered products and reveal changing patterns of products with changing decomposition conditions. The results are summarised in Table 3.

With the exception of the nitro compounds, the major products were ring-expanded 10*H*-azepinoindoles (**23**–**27**) and substituted aminodiphenylmethanes. Minor quantities of acridines and acridans were also found particularly from the azide **3d** which also yielded a tetracyclic compound identified as 1a,9b-dihydro-1*H*-cyclopropa[1′,2′:3,4]pyrido[1,2-*a*]indole (**28**) (see below). Compounds **23** and **25** from azides **3a** and **3c** have been reported by us previously.[19,7] The new azepinoindoles **24** and **26** from azides **3b** and **10** were identified by their ^{1}H NMR absorptions at δ 2.3 (3 H, s), 3.25 (2 H, d, 10-H_2), 5.3–5.9 (4 H, m, 7-, 8-, 9-, 11-H and 6.6–7.8 (4 H, m, 1-, 3-, 4-, 6-H), and at δ 3.3 (2 H, d, 10-H_2), 3.7 (3 H, s, OCH_3), 5.4–5.9 (4 H, m, including 11-H singlet at δ 5.9) and 6.5–7.2 (characteristic pattern of 5-methoxyindole), respectively.

Analysis (GLC) of the reaction mixtures from decompositions of the mononitro compound **15** showed four products to be present. Isolation and identification of three of these (about 66% of total product yield) was not achieved. The ^{1}H NMR spectrum of a mixture of two of these compounds indicates that they are of the ring-expanded type. The fourth product was found to be azepino[1,2-*a*]indol-8-one (**32**), identical with a previously prepared specimen.[2] The amine **14** was absent from the crude mixture (GLC).

No reaction products were isolated from the dinitro-substituted azide **18**.

Gas chromatographic examination of the crude products of decomposition of the azide **3d** showed six peaks (compounds **A** to **F**) of which five (**B** to **F**) have been identified, together with a sixth product not present in the crude mixture. Product **A** was present in *ca.* 1% yield according to gas chromatographic analysis, but was not isolated in any of the column chromatography fractions. The products were separated by chromatography on alumina, and are described in order of elution, with the gas chromatography identifying letter given in parentheses.

First from the column (peak **D**) was a pale yellow compound readily identified as the azepinoindole **27**, previously reported.[2] The azepinoindole **27** and the next compound eluted (peak **B**) were the major components at all temperatures although their relative proportions varied. The ^{1}H NMR spectrum of the new compound, which we believe to have structure **28** was strikingly different from that of the azepinoindole **27** although the two

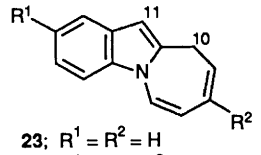
Table 3 Product yields from the decomposition of 2-azidodiarylmethanes

T/°C	c/mol dm^{-3}	Azepinoindole (%)	Aminodiphenyl methane (%)	Ratio	Total (%)	Tetracyclic cpd. (%)	Acridine + acridan (%)	Other compounds
2-Azidodiphenylmethane (**1**)								
163.0	0.18	46.2	5.7	8.1	51.9			
163.0	0.15	45.0	18.0	2.5	63.0			
168.0	0.12	64.4	20.0	3.2	80.4			
168.0	0.20	60.4	26.4	2.3	86.8			
168.0	0.40	60.5	21.8	2.8	82.3			
173.0	0.26	75.4	12.9	5.8	88.3			
173.0	0.29	65.5	22.8	2.9	88.3			
185.0	0.15	56.7	17.9	3.2	74.6			
185.0	0.16	50.1	28.7	1.7	78.8			
185.0	0.18	52.0	19.1	2.7	71.1			
2-Azido-4′-methyldiphenylmethane (**3c**)								
163.0	0.07	51.4	10.9	4.7	62.3			
168.0	0.15	41.9	12.7	3.3	54.6			
170.0	0.10	26.0	14.5	1.8	40.0			
173.0	0.14	41.3	13.1	3.1	54.4			
180.0	0.10	30.0	13.3	2.3	43.0			
185.0	0.10	19.0	12.1	1.6	31.0			
185.0	0.14	49.0	11.1	4.4	60.1			
2-Azido-4′-methoxydiphenylmethane (**3d**)								
160.0	0.13	56.6	32.0	1.8	93.1	1.1	3.4	
160.0	0.20	15.3	33.2	5.2	86.2	20.8	17.9	
163.0	0.17	21.8	8.7	8.7	92.8	54.4	7.9	
173.0	0.15	35.4	3.2	25.2	87.5	45.3	3.6	
175.0	0.14	27.0	15.2	4.1	85.2	35.0	8.0	
180.0	0.21	22.6	34.5	1.0	66.5	12.9	0.0	
180.0	0.20	22.0	30.0	1.3	81.4	18.0	11.4	
180.0	0.20	59.9	16.2	4.9	96.2	20.1	0.0	
185.0	0.13	44.8	2.2	38.6	89.8	40.1	2.7	
2-Azido-5-methyldiphenylmethane (**3b**)								
150.0	0.24	46.3	27.3	1.7	73.6			
150.0	0.20	46.8	21.1	2.22	69.9			
160.0	0.15	47.2	29.6	1.60	76.8			
160.0	0.16	45.8	30.1	1.52	75.1			
170.0	0.18	48.3	25.4	1.90	73.7			
170.0	0.16	44.1	29.4	1.50	73.7			
182.0	0.16	32.5	36.2	0.90	68.9			
182.0	0.10	39.4	46.8	0.63	76.2			
2-Azido-5-methoxydiphenylmethane (**10**)								
145.3	0.07	17.3	30.2	0.57	47.5			
150.0	0.07	33.8	43.8	0.77	77.6			
150.0	0.09	34.0	29.6	1.15	63.6			
160.0	0.07	33.5	26.9	1.25	60.4			
160.0	0.06	26.6	29.6	0.90	56.2			
170.0	0.09	21.1	24.8	0.85	45.9			
170.0	0.06	21.5	30.2	0.71	51.9			
2-Azido-4′-nitrodiphenylmethane (**15**)								
160.0	0.05	17.3			54.7			37.4
160.0	0.04	15.7			75.3			59.5
170.0	0.07	26.0			83.3			57.3
170.0	0.09	30.5			73.8			43.3
180.0	0.09	32.8			75.5			42.7
180.0	0.01	29.4			74.0			44.6
185.0	0.01	17.2			68.5			51.3
185.0	0.01	31.6			79.3			47.7

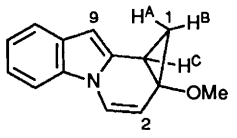
were isomers. Outstanding signals were an ABM system at δ 0.5 (1 H, t, 1-H^A), 1.8 (1 H, dd, J = 5 and 10.5 Hz, 1-H^B) and 2.7 [1 H, ddd, J = 1.5, 5 and 10.5 Hz, 9b-H (H^C)] characteristic of a fused cyclopropane ring, the methoxy signal at δ 3.35, a doublet of doublets (1 H) at δ 5.7 (J = 1.5 and 10 Hz, 2-H), and the indole (9-H) proton at δ 6.45 (s). The spectrum was very similar to that of the 9-(*p*-methoxyphenyl) derivative previously reported;[4] the long-range coupling from 2-H to 9b-H is particularly clear. The third compound was eluted from the column as an intense yellow band and was shown by its ^{1}H NMR spectrum to be 9,10-dihydroazepino[1,2-*a*]indol-8-one (**29**).[2] Examination of its retention time on the gas chromatograph showed that this compound is not present in the crude mixture, and we believe that it is an artefact, formed by hydrolysis of the azepinoindole **27** (a known[2] reaction). The last three products from the column were 2-methoxyacridan

(**30**) (peak **E**), the amine **2d** (peak **C**) and 2-methoxyacridine (**31**) (peak **F**). The acridan **30** was identified by comparison with a synthetic specimen, and the acridine **31** by comparison of its NMR spectrum with that in the literature.[20]

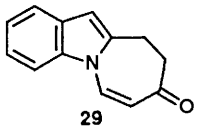
The deuteriated azides **21** and **22** were decomposed for 3 h at 453 and 448 K, respectively, and the reaction products isolated using an alumina column deactivated with D_2O. The content and position of the deuterium atoms in the products was estimated from their ^1H and ^2H NMR spectra. The methyl-substituted azide **21** gave the expected dideuteriated amine **19** and a mixture of azepinoindoles **25** having full deuteriation at the methine C-11 atoms and *ca.* 25% deuterium at the methylene C-10 atoms. No deuterium was found at C-9. The methoxy-substituted azide **22** gave the dideuteriated amine **20**, acridine and acridan products and azepinoindole **27**, deuteriated at C-9 and C-10 in the ratio *ca.* 2:1 as well as at C-11. In the tetracyclic compound **28** the C-9 (the indole β carbon) position was deuteriated and the ^2H NMR signal for the *exo* and *endo* positions of the cyclopropane each showed integrals of *ca.* 0.3 deuterium atoms. Decomposition of this tetracycle yielded the azepinoindole **27** with deuteriation at C-9 and C-10 in the ratio *ca.* 2:1.



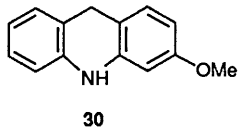
23; $R^1 = R^2 = H$
24; $R^1 = Me$, $R^2 = H$
25; $R^1 = H$, $R^2 = Me$
26, $R^1 = OMe$, $R^2 = H$
27; $R^1 = H$, $R^2 = OMe$



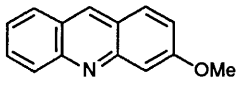
28



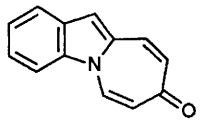
29



30



31



32

The yields of major products recovered and the ratio of azepinoindole to amine, given in Table 3, show considerable scatter, and no correlation between yields and reaction conditions (temperature and initial concentration) is observed. In general the *ratio* of amine to azepinoindole increases with the increase in electron-withdrawing nature of the 5-substituent. Attempts to account for variations in yields by addition of impurities (O_2 or N_2) to the carrier gas or of water to the solvent were unsuccessful. While the possibility of wall reactions cannot be ruled out, some of the discrepancies in the yields of products can be attributed to inherent analytical difficulties. The evaporation of the trichlorobenzene solvent before the GLC analysis (necessary owing to its interference in the GLC trace), and the potential for decomposition or rearrangement on the column are perhaps the most likely reasons for the very variable amounts of products isolated. The consistently good first-order plots from the kinetic analysis and the reproducible values for k, found despite variable product yields, indicate that the decomposition to nitrene is rate determining.

Rate Constants from NMR Spectra.—The rates of azide loss and of product formation in the decompositions of the 4′-methyl (**3c**) and 4′-methoxy (**3d**) azides were followed by monitoring the changes in the ^1H NMR spectra of the reaction mixtures at 448 and 433 K, respectively.

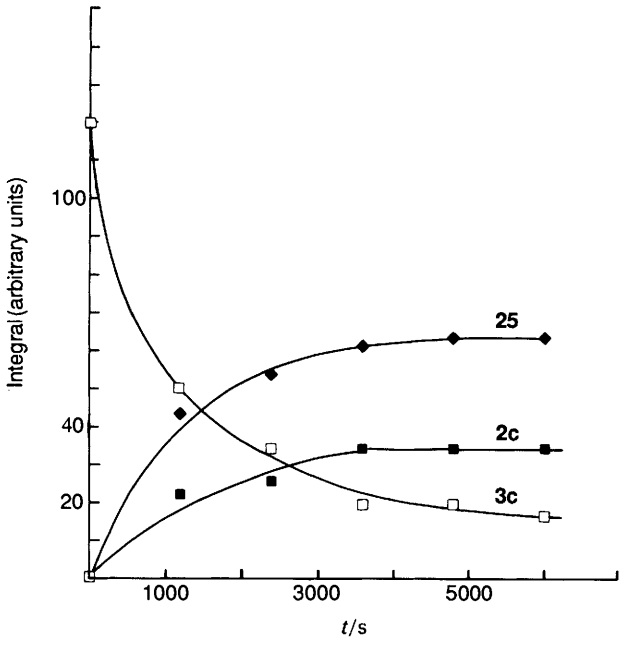


Fig. 1 NMR kinetic analysis of the azide **3c**, azepinoindole **25** and amine **2c** in reaction mixtures from the decomposition of 2-azido-4′-methyldiphenylmethane (**3c**) in trichlorobenzene at 448 K

For the azide **3c** the concentration of 8-methylazepinoindole **25** was determined directly from the integral of its methyl singlet at $\delta = 1.7$. A multiplet at $\delta = 3.3$ containing the C-10 doublet of the 8-methylazepinoindole overlapping the NH_2 signal of the amine and a singlet at $\delta = 2.2$ due to the methyl groups of the amine and azide were then used to calculate the concentrations of amine and azide in the reaction mixtures. The spectra of the decomposition mixtures from the azide **3d** gave less good base lines partly because of the necessarily high amplification. However, distinct signals at $\delta = 3.5$ and 3.3 for the methoxy groups on the azide **3d**, and 8-methoxyazepinoindole **27**, respectively, and a signal at 3.1 ppm composed of contributions from the methoxy signal from the tetracycle **28** and from the C-10 protons of azepinoindole **27** were used to estimate the concentrations of each of these three compounds.

For both sets of data, plots of concentration of the various species against time gave smooth curves (Figs. 1 and 2). Non-linear least-squares analyses of the data for the azides and ring-expanded products gave good first-order plots and rate constants which agree reasonably well with those found from nitrogen evolution (Table 4). The first-order plot for the data for formation of 4′-methoxy-2-aminodiphenylmethane (**2d**) showed greater scatter and gave a lower value for the rate constant than those for the azide **3d** and azepinoindole **27**. This probably reflects the difficulties in estimating the size of the NH_2 integral rather than indicating that the rate-determining step for the formation of this product is not the loss of nitrogen. Underestimation of the amine signal also leads to overestimation of the azide, making the measured 'infinity value' (at 100 min) higher than the rate constant indicates. The first-order rate constants were obtained by estimating the infinity value using an iterative method; thus scatter in the amine values will influence the calculated rate constant.

The tetracyclic compound **28** rearranges on heating to the azepinoindole **27**. The rate constant for this process was estimated using the change with time in the size of the methoxy signals from each of the two compounds at $\delta = 3.1$ and $\delta = 3.25$ in the NMR spectra of a solution of the tetracycle **28**

Table 4 Rate constants ($k/10^{-4}$ s) determined by NMR spectroscopy

T/°C	Reactant/product analysed	k from NMR analysis	k from N_2 data
From compound **3c**			
175	2-Azido-4′-methyldiphenylmethane (ln $A - A_0$)	8.68	9.00
	8-Methylazepinoindole (ln $A_\infty - A$)	9.28	9.00
	2-Amino-4′-methyldiphenylmethane (ln $A_\infty - A$)	5–7.3	
160	2-Azido-4′-methyldiphenylmethane (ln $A - A_0$)	2.1	2.8
From compound **3d**			
160	2-Azido-4′-methoxydiphenylmethane (ln $A - A_0$)	2.4 ± 0.3	2.9
	8-Methoxyazepinoindole + 1a-methoxy-1a,9b-dihydro-1*H*-cyclopropa[1′,2′:3,4]pyrido[1,2-*a*]indole	3.4 ± 0.3	2.9

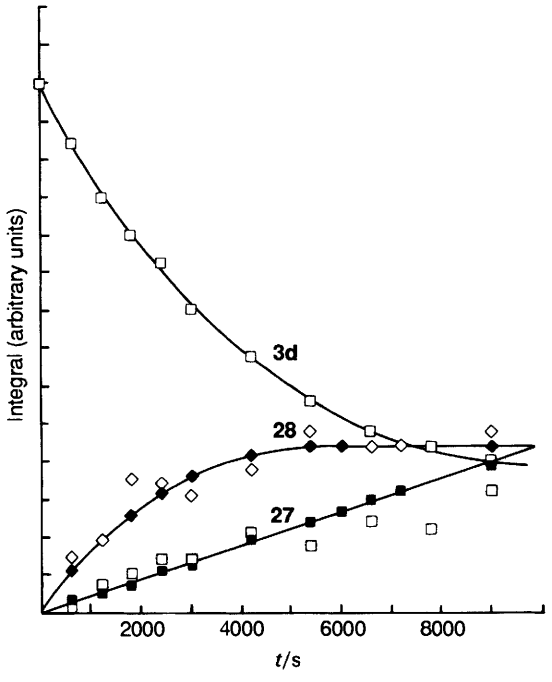


Fig. 2 NMR kinetic analysis of the azide **3d**, tetracyclic compound **28** and azepinoindole **27** in reaction mixtures from the decomposition of 2-azido-4′-methoxydiphenylmethane (**3d**) in trichlorobenzene at 433 K. Open symbols indicate experimental values; filled symbols and curves represent calculated values.

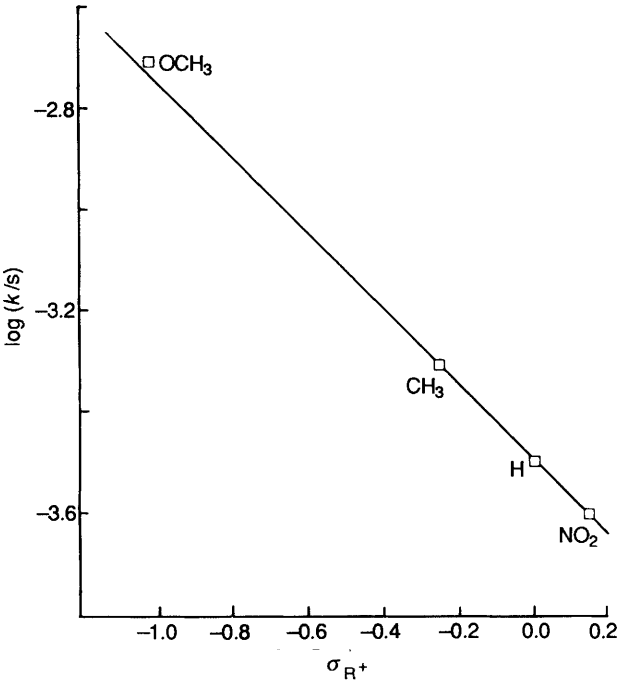


Fig. 3 log (k/s) against σ_{R^+} for decomposition of 5-substituted 2-azidodiarylmethanes in trichlorobenzene at 433 K

heated in trichlorobenzene. Monitoring of the signal at 3.1 ppm from compound **28** was complicated by the appearance of the 2 H doublet (C10) of the azepinoindole **27** and it was necessary to correct the integral for this. These analytical difficulties mean that the rate constants derived from these results are only accurate to about ±20%. Nevertheless they indicate that the rearrangement **28** ⟶ **27** is slower than the direct formation of the tetracycle **28** from azide **3d**. The average value of k is used in the calculations below.

Discussion

Evidence for Nitrene Formation as the Rate-determining Step.—Our kinetic results provide confirmation of our earlier assumption that the initial and rate-determining steps in the decomposition of 2-azidodiarylmethanes is nitrene formation with subsequent fast product-forming reactions, in the following ways.

(i) Substitution at the 4′-position affects the product yields, but has no appreciable effect upon decomposition rates while 5-substitution results in rate changes indicating that breaking of the azide bonds is rate determining. The rate constants determined from NMR measurements of product formation (Table 4), are substantially the same as those found from nitrogen evolution analyses, providing qualitative corroborating evidence.

(ii) For the 5-substituted compounds, the methoxy substituent has much greater influence on the decomposition rate than would be expected from a consideration of the σ or σ^+ substituent constants. While the log k values for **3a**, **3b** and **18** decrease approximately linearly with increasing σ values (R = 0.87 ρ = −0.3) that for **10** falls well above the line. Using σ^+ constants gives no better correlation. In plotting these points we have assumed that rate retardation found in compound **18**, which is substituted at both 5- and 4′-positions is due solely to the 5-NO_2 substituent, since substitution at 4′ only (compound **15**) has no effect on the rate (Table 1). Compound **18** was used because, as mentioned in the synthesis section, mononitration at the 5-position only could not be achieved. The unusually high contribution of the methoxy substituent to the rate indicates formation of an electron deficient species, stabilised by resonance rather than induction. The excellent linearity (R = 0.99) of the plot of log k against σ_{R^+}, for all the 5-substituted compounds (σ_{R^+} = −0.78 at 433 K) provides further indication that this is so (Fig. 3).

The retardation by the nitro group in these decompositions contrasts with decompositions in decalin of phenyl azides and 2-azidobiphenyls,[12,8] where all *para* substituents are reported to increase decompositions rates. On the other hand, decompo-

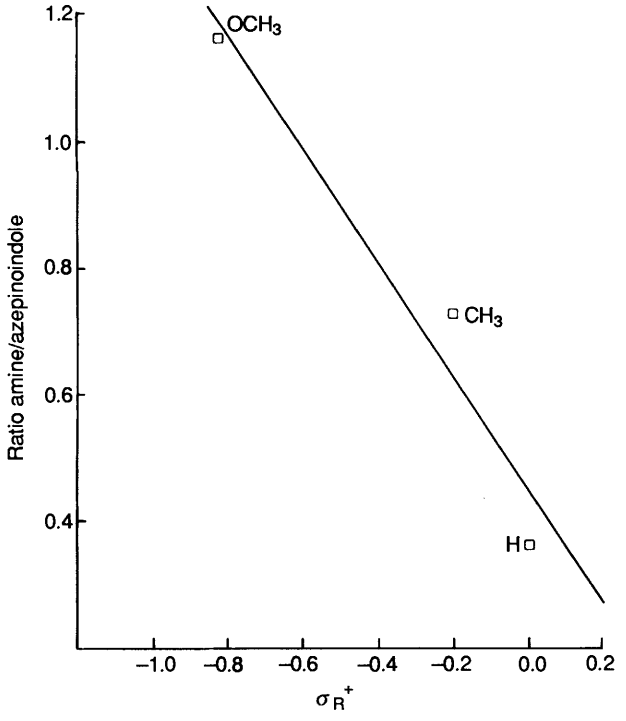


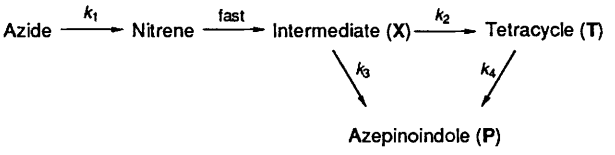
Fig. 4 Ratio of amine to azepinoindole products against σ_R^+ from decompositions of 5-substituted 2-azidodiarylmethanes in trichlorobenzene at 433 K

sition rates of 4-substituted 2-nitrophenyl azides do obey the Hammett equation with a small ρ value[22] which Dyall has interpreted as indicating little singlet nitrene character in the decompositions.

(iii) Resonance stabilisation by the 5-methoxy substituent results in an enthalpy of activation which lies below the straight line $\Delta H^{\ddagger} = 402.2\Delta S^{\ddagger} + 1.352 \times 10^5$ (R 0.99) shown by the other compounds. For 2-azidobiphenyls $\Delta H^{\ddagger}$ also increases slightly with decrease in electron donation of *para* (but not *meta*) substituents, and Smith[8] has attributed this to conjugation with the azido group, despite there being no simple Hammett correlation. The large and negative values of the activation entropies for all except the dinitro compound, are similar to those found by Dyall for phenyl azide decompositions.[12] It is unlikely that they arise from major changes in the configuration of the reactant on going from the ground to the transition state and are probably due to changes in solvation at the reaction centre, which vary with the degree of stabilisation of negative charge on the nitrogen atom.

Product Formation.—Results in Table 3 indicate that the subsequent reactions of the nitrenes are sensitive to conditions, although the scatter in the experimental data may arise from reactions occurring on the columns during analysis. With the exception of the one or two anomalous values, the ratio of amine to azepinoindole products is approximately constant, within the limits of the (large) experimental error, for each of the compounds **1**, **3b** and **10**. The average values, *viz.*, 0.30, 0.67, 1.12, respectively, parallel the change in resonance electron density at the nitrogen as measured by the σ_R^+ constants (Fig. 4). If amine formation arises from a relatively slow spin-forbidden singlet-to-triplet transition in the nitrenes, as we have earlier proposed, those nitrenes which are most stabilised by substituents would be expected to have longest lifetimes and thus to give rise to highest yields of triplet products. Similarly, absence of resonance stabilisation in the nitro compound **18** leads to a very short nitrene lifetime, resulting in intractable tars from its vigorous reactions. Tar formation is also reported from thermolysis of *p*-nitro-substituted phenyl azides in acetic anhydride and benzoyl chloride.[23] With compounds **3c** and **3d**, the ratio of amine to ring-expanded products appears to increase as the total yield of these products increases in the decompositions. This increase is less easily accounted for and may indeed be an artifact of the experimental techniques.

The formation of the tetracyclic compound 1a-methoxy-1a,9b-dihydro-1*H*-cyclopropa[1′,2′:3,4]pyrido[1,2-*a*]indole (**28**) from the azide **3d** has not hitherto been reported. Cliff and Jones[2] decomposed the azide **3d** using very low initial concentrations and taking the reaction to completion; they do not report finding the tetracycle **28**. On being heated, it rearranges slowly to the 8-methoxyindole **27** and is probably a stable intermediate in the formation of compound **28** during the thermal decomposition of the azide **3d**. The rate constant for the rearrangement **28** ⟶ **27** is slower than that for decomposition of the azide **3d** thus accounting for its presence in the reaction products. The presence of the tetracycle **28** does not rule out formation of the azepinoindole **27** by a second, competing process which does not require the intermediacy of the tetracyclic compound **28**. Indeed it is to be expected that this second route is operative, since the other azides form azepinoindoles without apparently going through a tetracyclic intermediate. As a test of this hypothesis we can set up the mechanism shown below, and, using the experimental values for the rate constants, we can calculate expected values for the concentrations of the tetracyclic compound and azepinoindole during the course of a reaction, for comparison with experimental observation. Assuming Scheme 5 to be operative, then, if



Scheme 5

$k_3 = 0$, the mechanism is two first-order, consecutive reactions and the concentrations of **T** and **P** are given by[24] eqns. (1) and (2) where $[A]_0$, the initial azide concentration, replaces $[X]_0$,

$$[T]_t = [A]_0(k_2)/(k_4 - k_2)\,\exp(-k_2t) - \exp(-k_4t) \quad (1)$$

$$[P]_t = [A]_0 + [A]_0[k_4\exp(-k_2t) - k_2\exp(-k_4t)]/(k_2 - k_4) \quad (2)$$

and k_2 may be replaced by k_1, since **X** is formed by fast reaction of the nitrene.

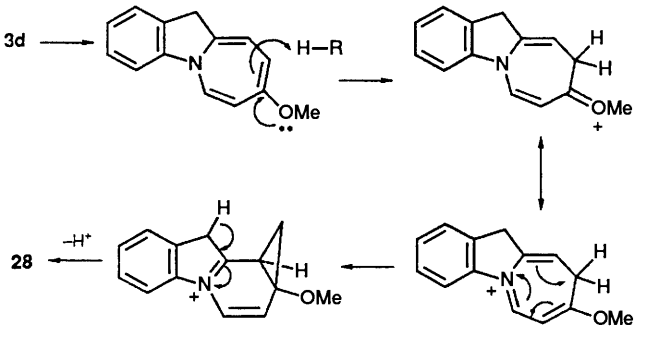
Using the experimental values at 433 K of $k_2 = 2.9 \times 10^{-4}$ s^{-1}, $k_4 = 8 \times 10^{-5}$ s^{-1}, and $[A]_0 = 39$ integral units (the experimental value, 50 multiplied by 0.78 to account for the proportion of azide yielding other products), calculated values for [**T**] and [**P**] were plotted against time. The curve for [**T**] matched the experimental curve fairly well, showing a maximum of 23 integral units at about 100 mins, though the values for the earlier stages of the reaction were all a little higher than the experimental values. The match for [**P**] was poor, with the calculated values for the earlier part of the reaction being very much lower than the experimental. It appeared then that $k_3 \neq 0$, and that the azepinoindole was indeed being formed by two processes.

The initial rates of formation of azepinoindole and tetracyclic compounds can be estimated from the experimental curves to be in the ratio of 1:4, so that as a first approximation k_2 may be replaced by 0.8 k_1 in eqn. (1) and $[P]_t$ in eqn. (2) must be increased by $0.2[A]_0[1 - \exp(-k_1t)]$. The calculated values for $[T]_t$ and $[P]_t$ using these data, shown in Fig. 2 (solid curves),

give a slightly improved fit for the tetracycle **28**, and also correlate well with the experimental data for the concentration of the azepinoindole **27**. The routes for formation of 8-methoxyazepinoindole **27**, are therefore clearly demonstrated to be both rearrangement of the tetracyclic compound and direct formation from the intermediate **X**. The involvement of the tetracyclic compound is confirmed by the results from the decomposition of the deuteriated azides **21** and **22**.

We have previously suggested [2] that the nitrene intermediates in these reactions give rise first to 11*H*-azepinoindoles which rearrange to the 10*H*-isomers and this explains the presence of deuterium at the C-10 position in azepinoindoles obtained from the deuteriated azides **21** and **22**. Deuterium at C-9 in the 8-methoxyazepinoindole from the azide **22** must arise *via* a different route involving the tetracycle as an intermediate. These deuterium estimations were obtained by using ^{2}H NMR spectra, so that labelled positions were easily identified.

We believe that the transfer of the hydrogen atom from the original methylene group in the azide to the tetracycle cannot be concerted since the *exo* and *endo* positions are equally labelled. An inspection of models shows that if the rearrangement could occur by some unusual 1,4-sigmatropic procedure, only one hydrogen atom could make the required suprafacial transfer. A mechanism is shown in Scheme 6 which uses a proton abstraction to initiate the conversion of the first-formed 11*H*-azepinoindole into the tetracycle, but a hydrogen radical abstraction mechanism would be equally applicable. The presence of the methoxy group at the eventual position **1a** of the tetracycle is necessary to stabilise the intermediate ion (or radical) prior to the electrocyclic reaction which forms the tetracyclic compound **28**.

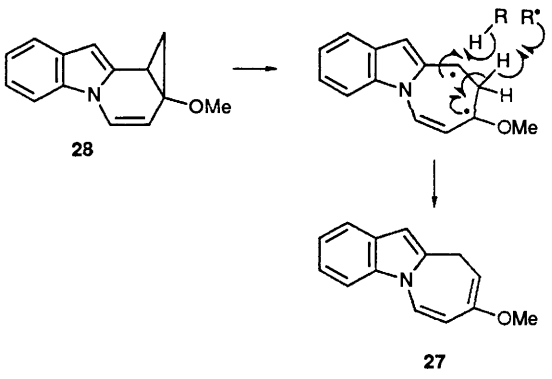


Scheme 6

The conversion of the tetracycle **28** into the azepinoindole **27** is equivalent to the thermolysis of a vinylcyclopropane, an area much studied and reviewed.[25] The general consensus favours a diradical intermediate, formed by homolytic cleavage of one bond in the cyclopropane ring, and this process is known to be favoured by attachment of an electronegative atom to the cyclopropane ring. There are few examples of cyclopropanes fused to cyclohexanes with a conjugated double bond; in the examples with fused seven-membered rings the ring expansion is combined with 1,5 shifts which are not possible in our, more unsaturated, system. We assume that the ring expansion is followed by hydrogen abstraction from the partially deuteriated methylene group of another molecule, thus accounting for the presence of some deuterium at position 10 in the azepinoindole (Scheme 7).

Experimental

M.p.s were recorded on a Kolfer heated stage and are uncorrected. NMR spectra were determined for $CDCl_3$ solutions unless otherwise stated. Alumina was Merck, the degree of deactivation being shown thus (IV). PLC and Chromatotron separations used silica as the stationary phase (Merck PF_{254}).



Scheme 7

2-Amino-5-methylbenzophenone (**1b**) *and 2-Acetamido-5-methylphenyl(diphenyl)methanol*(**4**).—Reaction between phenylmagnesium bromide and 6-methylacetanthranil by our standard procedure [2] gave a crude product which was separated by chromatography on neutral alumina (activity IV). Elution with toluene gave the acetyl derivative of compound **1b**, hydrolysed to the amine **1b** with boiling ethanol–concentrated hydrochloric acid (2 h). Neutralisation of the acid solution, and purification by recrystallisation from ethanol gave pure amine **1b** (15% yield), m.p. 59–61 °C (lit.,[15] m.p. 62 °C, lit.,[16] m.p. 60 °C) (Found: C, 79.75; H, 6.1; N, 6.4. Calc. for $C_{14}H_{13}NO$: C, 79.6; H, 6.15; N, 6.65%); δ_H 2.2 (3 H, s), 5.7 (2 H, br s, NH_2) and 6.6 (1 H, d, 3-H), 6.9–7.7 (7 H, m). Further elution of the column using ethyl acetate gave the *triarylmethanol* **4** (33% yield) (from ethyl acetate) (Found: C, 79.65; H, 6.6; N, 4.45. $C_{22}H_{21}NO_2$ requires C, 79.75; H, 6.4; N, 4.25%); *m/z* 331 (M^+, 100%), 271 ($M - CH_3CO_2H$, 33%), 270 (60%); δ_H 1.55 (3 H, s), 2.15 (3 H, s), 6.45 (1 H, br s, OH), 7.2–7.5 (12 H, m), 7.9 (1 H, d, 3-H) and 8.8 (1 H, br s, N*H*$COCH_3$).

Nitration of 3-Methoxydiphenylmethane (**5**).—(*a*) A solution of acetyl nitrate, prepared by slow addition of concentrated nitric acid (20 cm^3) to acetic anhydride (100 cm^3) (under nitrogen at 5 °C) was added slowly to a well stirred solution of 3-methoxydiphenylmethane (**5**) (45 g) in glacial acetic acid (130 cm^3) at 0 °C. The stirred mixture was allowed to reach room temperature over 4 h. The mixture was poured into distilled water (4 dm^3), extracted with ethyl acetate, dried ($MgSO_4$) and evaporated to give a pale yellow semisolid residue. The crude residue was partly separated by chromatography on alumina (IV, 700 g). Elution with light petroleum (b.p. 40–60 °C) gave unchanged 3-methoxydiphenylmethane (0.5 g), then two products unresolved (fraction A); elution with ethyl acetate gave *3-methoxy-4-nitrodiphenylmethane* (**7**) m.p. 75–76 °C (from light petroleum–ethyl acetate) (11.9 g, 49%) (Found: C, 69.05; H, 5.3; N, 5.8. $C_{14}H_{13}NO_3$ requires C, 69.1; H, 5.4; N, 5.75%); δ_H 3.8 (3 H, s), 4.0 (2 H, s), 6.75 (1 H, d, 6-H, J = 8 Hz), 6.8 (1 H, br s, 2-H), 7.2 (5 H, br s) and 7.65 (1 H, d, 5-H, J = 8 Hz); δ_C 41.8 (t, CH_2), 56.15 (q, OCH_3), 113.6 (d, C-2), 120.4 (d, C-6), 125.7 (d, C-4′), 126.4 (d, C-5), 128.4 (d, C-2′, 6′), 128.6 (d, C-3′, -5′), 137.3 (s, C-4), 138.9 (s, C-1′), 148.6 (s, C-1) and 152.8 (s, C-3). The residues from the light petroleum fractions were redissolved in acetone and the acetone allowed to evaporate off for 24 h. One compound formed large regular crystals, and was separated from the residual oil, washed with hot light petroleum (b.p. 40–60 °C) and found to be almost pure *3-methoxy-2-nitrodiphenylmethane* (**6**) m.p. 104–106 °C (from light petroleum–ethyl acetate) (5.5 g, 23%) (Found: C, 69.5; H, 5.3; N, 5.6. $C_{14}H_{13}NO_3$ requires C, 69.1; H, 5.4; N, 5.75%); δ_H 3.8 (3 H, s, OCH_3), 3.9 (2 H, s), 6.65–6.9 (3 H, m, 4-H, 5, 6) and 7.2 (5 H, br s); δ_C 36.53 (t, CH_2), 56.34 (q, OCH_3), 110.4 (d, C-4), 122.2 (d, C-6), 126.7 (d, C-4′), 128.6 (d, C-2′, -6′), 129.0 (d, C-3′, -5′), 130.8

(d, C-1), 133.9 (s, C-2), 138.2 (s, C-1′) and 150.7 (s, C-3). The residual oil (more than 90% compound **8**) was run slowly through a column of alumina, eluting with light petroleum (b.p. 40–60 °C), pure fractions (by GLC) were combined and evaporated to give 5-methoxy-2-nitrodiphenylmethane (**8**) (3 g, 12%) as an oil; δ_H 3.75 (3 H, s), 4.35 (2 H, s), 6.65–6.85 (2 H, m), 7.2 (5 H, m) and 8.0 (1 H, d, 3-H, J = 8 Hz); δ_C 39.06 (d, CH_2), 55.49 (q, OCH_3), 111.6 (d, C-4), 117.5 (d, C-2), 126.2 (d, C-5), 127.5 (d, C-4′), 128.2 (d, C-2′, -6′), 128.6 (d, C-3′, -5′), 138.5 (s, C-1), 138.7 (s, C-1′), 141.6 (s, C-6) and 162.8 (s, C-3).

2-*Amino-5-methoxydiphenylmethane* (**9**).—A mixture of palladium-on-charcoal (10%, 1 g) and 2-nitro-5-methoxydiphenylmethane (**8**) (1 g) and cyclohexene (6 cm^3) in 95% ethanol (50 cm^3) was boiled under reflux (1 h). The cooled solution was filtered and evaporated and the solid residue was recrystallized to give the amine[25] **9** (0.8 g, 91%) (Found: C, 78.95; H, 7.1; N, 6.55. Calc. for $C_{14}H_{15}NO$: C, 78.85; H, 7.05; N, 6.55%); δ_H 3.3 (2 H, br s, NH_2), 3.6 (3 H, s), 3.8 (2 H, s), 6.45–6.75 (3 H, m) and 7.15 (5 H, m).

2-*Acetamido-4′-nitrodiphenylmethane* (**13**).—Nitration of 2-acetamidodiphenylmethane as described by Davies *et al.*[17] gave, in 54% yield, a compound that recrystallised from acetone, m.p. 198 °C (lit.,[17] m.p. 200 °C) said to be 2-acetamido-5-nitrodiphenylmethane. Our NMR data showed this compound to be 2-acetamido-4′-nitrodiphenylmethane (**13**); δ_H 1.9 (3 H, s, $NHCOCH_3$), 4.05 (2 H, s), 6.9–7.4 (6 H, m), 8.0 (2 H, d, J = 8 Hz, 3′-, 5′-H) and 9.3 (1 H, br s, $NHCOCH_3$).

2-*Amino-4′-nitrodiphenylmethane* (**14**).—The amide **13** (6.3 g) was hydrolysed with boiling concentrated hydrochloric acid (68 cm^3) and acetic acid (13.6 cm^3) (6 h). Basification, extraction (CH_2Cl_2), drying ($MgSO_4$) and evaporation gave the amine **14**, recrystallised from ethanol m.p. 100–102 °C (lit.,[17] 104–105 °C for the compound described as 2-amino-4-nitrodiphenylmethane) (4.03 g, 76%) (Found: C, 68.15; H, 5.3; N, 12.25. Calc. for $C_{13}H_{12}N_2O_2$: C, 68.4; H, 5.25; N, 12.3%); m/z 228 (M^+); δ_H 3.5 (2 H, br s, NH_2), 3.9 (2 H, s), 6.5–7.1 (4 H, m), 7.2 (2 H, d, 2′-, 6′-H) and 8.0 (2 H, d, 3′-, 5′-H).

2-*Amino-4′,5-dinitrodiphenylmethane* (**17**).—Powdered 2-acetamidodiphenylmethane (**12**) (10 g) was added slowly to a well stirred mixture of concentrated nitric acid (10 g) and concentrated sulfuric acid (5 g), the temperature being kept below 20 °C. The mixture was then heated (60 °C, 1 h) and then poured into iced water (300 cm^3). A pale yellow precipitate was formed. The mixture was left overnight and then filtered and the solid material was shaken with dichloromethane and again filtered. The product was hydrolysed as described for the mononitro compound **8**. The *aminodinitrodiphenylmethane* **17** had m.p. 193 °C (from acetone). More material was recovered from the dichloromethane washings, by chromatography on alumina column (IV) eluting with a mixture of dichloromethane and toluene (1:1). The total yield was 2.3 g (17.6%) (Found: C, 57.05; H, 3.95; N, 15.35. $C_{13}H_{11}N_3O_4$ requires C, 57.15; H, 4.05; N, 15.4%); m/z 273 (M^+, 100%), 243 (23), 180 (43); δ_H[$(CD_3)_2SO$] 3.95 (2 H, s), 5.4 (2 H, br s, NH_2), 6.7 (1 H, d, J = 8 Hz, 3-H), 7.25 (2 H, d, 2′-, 6′-H) 7.7–8.0 (2 H, m) and 8.1 (2 H, d, J = 8 Hz, 3-, 5-H).

2-*Amino-5-methyldiphenylmethane* (**2b**).—Prepared from 2-amino-5-methylbenzophenone (**1b**) in 78.5% yield by a procedure due to Engels, Lamchen and Wicken,[26,14] and used for similar compounds by us, b.p. 55–60 °C/0.7 mmHg (lit., b.p. 124–127 °C/10.27 mmHg[27] and 150–170 °C/10.1 mmHg[28]) (Found: C, 85.1; H, 7.7; N, 6.95. Calc. for $C_{14}H_{15}N$: C, 85.25; H, 7.65; N, 7.1%); δ_H 2.2 (3 H, s), 3.15 (2 H, br s, NH_2), 3.8 (2 H, s), 6.45 (1 H, d, 3-H) and 6.7–7.3 (6 H, m).

2-*Azido-5-methyldiphenylmethane* (**3b**).—The general procedure has been described,[16] using a mixture of dioxane and sulfuric acid as the solvent; the amine **2b** gave the *azide* **3b**, purified by column chromatography as an oil in 56.6% yield (Found: C, 75.65; H, 5.7; N, 18.6. $C_{14}H_{13}N_3$ requires C, 75.3; H, 5.85; N, 18.8%); δ_H 2.1 (3 H, s), 3.75 (2 H, s), 6.7–6.9 (3 H, m) and 7.1 (5 H, m).

2-*Azido-5-methoxydiphenylmethane* (**10**).—Similarly prepared from the amine **9** in 42% yield was the *azide* **11** as an oil (Found: C, 70.45; H, 5.6; N, 17.5. $C_{14}H_{13}N_3O$ requires C, 70.25; H, 5.45; N, 17.55%); δ_H 3.5 (3 H, s), 3.7 (2 H, s) and 6.5–7.25 (5 H, m).

2-*Azido-4′-nitrodiphenylmethane* (**11**).—Prepared from the amine **14** in 66% yield, the *azide* **15** had m.p. 55–57 °C [light petroleum (b.p. 40–60 °C)] (Found: C, 61.35; H, 3.9; N, 21.8. $C_{13}H_{10}N_4O_2$ requires C, 61.4; H, 3.95; N, 22.0%); δ_H 3.8 (2 H, s), 6.7–7.3 (6 H, m) and 7.9 (2 H, d, J = 8 Hz, 3′-, 5′-H).

2-*Azido-4′,5-dinitrodiphenylmethane* (**18**).—Similarly prepared from 2-amino-4′,5-dinitrodiphenylmethane (**17**) (5.18 g); it was necessary to heat the mixture of amine, dioxane, and acid to 90 °C to ensure complete solution before cooling for diazotisation. The crude product was chromatographed (alumina, IV), eluting with toluene, and a persistent impurity was removed by dissolving the azide in ethyl acetate and shaking the solution with dilute sodium hydroxide. The *azide* **18** had m.p. 103–104 °C [light petroleum (b.p. 60–80 °C)–toluene] (5.46 g, 89%) (Found: C, 51.95; H, 2.9; N, 23.15. $C_{13}H_9N_5O_4$ requires C, 52.15; H, 3.05; N, 23.4%); m/z 299 (M^+, 4%), 179 (30), 178 (28), 92 (70) and 91 (100); δ_H 3.95 (2 H, s), 7.0–7.3 (3 H, m) and 7.85–8.1 (4 H, m).

2-*Amino-4′-methoxydiphenyl*($^2H_2$)*methane* (**19**).—To a stirred suspension of freshly sublimed aluminium chloride (15 g) in a solution of lithium aluminium deuteride (3 g) in anhydrous ether (75 cm^3) was slowly added at 0.5 °C a solution of 2-amino-4′-methoxybenzophenone (**1d**) (6.05 g) in ether (100 cm^3). The mixture was boiled under reflux for 30 min then allowed to cool (30 min). Moist ether (100 cm^3) was carefully added, and the whole mixture was poured slowly into distilled water (500 cm^3) in a large conical flask (**WARNING**: violent frothing occurs). The mixture was separated, and the aqueous layer extracted with ether (2 × 200 cm^3). The dried ($MgSO_4$) ethereal layer was evaporated, and the residue distilled, b.p. 121 °C/0.07 mmHg, to give the *dideuteriodiphenylmethane* **19** (5.4 g, 85%), m.p. 50–51 °C [light petroleum (b.p. 60–80 °C)] (Found: 78.15; H, 7.55; N, 6.5. $C_{14}{}^1H_{13}{}^2H_2NO$ requires C, 78.15; H, 7.95; N, 6.5%); m/z 215 (M^+, 100%), 214 (31), 200 (11) and 184 (15); δ_H 3.3 (2 H, br s, NH_2), 3.6 (3 H, s, OCH_3) and 6.4–7.1 (8 H, m). No signal visible at δ 2.7.

2-*Amino-4′-methyldiphenyl*($^2H_2$)*methane* (**20**).—Prepared in almost quantitative yield by a similar procedure, from 2-amino-4′-methylbenzophenone (**1c**). Characterised only by NMR spectroscopy, the crude material was used for the next stage.

2-*Azido-4′-methoxydiphenyl*($^2H_2$)*methane* (**21**).—Prepared as described for compound **3d** in 70% yield, m.p. 41–43 °C [light petroleum (b.p. 40–60 °C)], identical in all spectra with compound **3d**, but for the absence of a signal in the ^1H NMR spectrum at δ 3.6.

2-*Azido-4′-methyldiphenyl*($^2H_2$)*methane* (**22**).—Prepared as described for compound **3d** in 66% yield, m.p. 55 °C [light

petroleum (b.p. 40–60 °C)], identical in all respects with compound **3c**, except for the absence of a signal in the ^{1}H NMR spectrum at δ 3.75.

Kinetic Methods.—(*a*) *Nitrogen release.* A known quantity of azide (usually about 1.5×10^{-3} mol dm^{-3}) was added to distilled 1,2,4-trichlorobenzene (15 cm^3) heated to the reaction temperature in a flask through which helium was passed at the rate of 12 cm^3 min^{-1}. The gas was passed into the 5 cm^3 loop of a gas-sampling valve attached to a Pye 104 Gas Chromatograph, having a 130 mm × 3 mm column of loosely packed Chromasorb at a temperature of 50 °C and a katharometer detector. The gas in the loop was sampled regularly (usually every 6 min). A single peak after each injection corresponded to the nitrogen in the helium. Small quantities of other volatiles carried over in the gas flow were absorbed onto the column. During the initial equilibration period (approximately 10 min) the peaks increased in size. The peak areas subsequently decreased exponentially with time, as the rate of nitrogen release decreased. Areas were measured using a Shimadzu C-R3A data processor and ln (peak area) was plotted against time. The reaction mixtures were left in the constant-temperature bath until they had gone to completion when the products were analysed.

(*b*) *Product formation.* A solution (0.2 mol dm^{-3}) of azide in trichlorobenzene was divided equally between a number of 4 mm NMR tubes, filling each one to a depth of 4 cm. The 60 MHz ^{1}H spectrum of each sample upfield from δ = 5.6 (to eliminate solvent interference) was recorded before heating to ensure that the integral size of signals to be used for analysis was the same in each sample. The tubes were then connected in series by rubber tubing through which helium passed and were immersed to a depth of not less than 5 cm in a constant-temperature bath. One tube was removed from the bath after each 10 or 20 min interval, the reaction was quenched by immersing the tube in cold water and the tube was sealed with a cap. The ^{1}H NMR spectra (upfield of δ = 5.6) of all the samples were recorded at the same time, to minimise instrumental variations. No solvent or Me_4Si was added, the zero being set using an external indicator. Integration of the relevant peaks gave a measure of the change in concentration of reactant and products.

(*c*) *Conversion of the tetracycle* **28** *into the azepinoindole* **27**. A quantity (0.8 cm^3) of a 0.1 mol dm^{-3} solution of a pure sample of 1a-methoxy-1a,9b-dihydro-1*H*-cyclopropa[1′,2′:3,4]pyrido-[1,2-*a*]indole in trichlorobenzene was pipetted into a 4 mm NMR tube, filling it to a depth of approximately 4 cm. After ^{1}H NMR analysis of the contents, the tube was heated in a helium atmosphere in a constant temperature bath for 20 min, cooled rapidly, and the NMR spectrum recorded again. The tube was then replaced in the oil bath and the procedure repeated until consecutive spectra were identical.

Product Analysis.—The solvent was evaporated from the azide solutions from the kinetics experiments and the crude residue was then analysed by capillary GLC (OV1) using ethyl acetate as the solvent. A programme from 125–300 °C (10 °C min^{-1}) was suitable for all product mixtures except that from compound **3d**, which required a rate of 5 °C min^{-1}. The programme was finished by 5 min at 300 °C. Standard solutions of all identified products were prepared in ethyl acetate and used for calibration. Multiple runs were made for each product mixture, and the error is estimated to be ±0.1% based on absolute peak areas. Individual decompositions are described below.

Preparative separations were by alumina (IV) column chromatography, eluting with light petroleum (b.p. 60–80 °C), followed by increasing percentages of ethyl acetate.

Product ratios determined by NMR spectroscopy were estimated to be accurate to within ±3%, based on the worst cases for smaller peaks; estimates based on methoxy peaks are considerably better. Deuterium content and site were determined by a combination of ^{1}H and ^{2}H NMR spectra, the latter ensuring that all labelled sites could be identified.

2-*Azidodiphenylmethane* (**3a**).—Azide (3.7 g) gave the azepinoindole **23** (1.76 g, 55%) (eluent light petroleum) and 2-aminodiphenylmethane (0.65 g; 20%) (eluent ethyl acetate).

2-*Azido*-5-*methyldiphenylmethane* (**3b**).—Azide (0.794 g) gave the 2-*methylazepinoindole* **24**, m.p. 55 °C [light petroleum (b.p. 40–60 °C)] (0.33 g, 48%, eluted with light petroleum) (Found: C, 86.15; H, 6.5; N, 6.95. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.15%); *m*/*z* 195 (M$^+$, 100%) and 180 (62); δ_H 2.3 (3 H, s), 3.25 (2 H, d, *J* = 6 Hz), 5.3–5.9 (4 H, m, 7-, 8-, 9-, 11-H), 6.6–7.8 (4 H, m). Further elution using ethyl acetate gave the amine **2b** (0.174 g, 25%).

2-*Azido*-4′-*methyldiphenylmethane* (**3c**).—Azide (0.568 g) gave the azepinoindole **25** m.p. 59–60 °C [light petroleum b.p. 60–80 °C), identical with the product previously reported[7] [0.158 g, 32%, eluted with light petroleum b.p. 60–80 °C). The other identified product, eluted with ethyl acetate, was the amine **2c** (0.068 g, 13.5%).

2-*Azido*-4′-*methoxydiphenylmethane* (**3d**).—Azide (3.0 g) gave the azepinoindole **27** m.p. 95 °C [light petroleum (b.p. 60–80 °C)] (lit.,[2] m.p. 95.5 °C) [1.165 g, 44%, eluted in the first two 100 cm^3 fractions using light petroleum b.p. (60–80 °C)]. Further fractions from the petroleum eluate gave 1a-*methoxy*-1a,9b-*dihydro*-1H-*cyclopropa*[1′,2′:3,4]*pyrido*[1,2-*a*]*indole* (**28**), m.p. 67–68 °C [from light petroleum (b.p. 40–60 °C] (0.53 g, 20%) (Found: C, 79.55; H, 5.95; N, 6.5. $C_{14}H_{13}NO$ requires C, 79.6; H, 6.2; N, 6.65%); *m*/*z* 211 (M$^+$, 100%), 196 (M − CH_3, 40), 180 (M − CH_3O, 44) and 167 (76); δ_H 0.5 (1 H, dd, *J* = 5 and 5 Hz, 1-H^A), 1.8 (1 H, dd, *J* = 10.5 and 5 Hz, 1-H^B), 2.7 (1 H, ddd, 9b-H, *J* = 10.5, 5 and 1.5 Hz), 3.35 (3 H, s), 5.7 (1 H, 2-H, dd, *J* = 10 and 1.5 Hz), 6.45 (1 H, s, 9-H), 7.0–7.55 (5 H, m, 4-, 6-, 7-, 8-, 9-H). Further elution with 5% ethyl acetate in light petroleum gave an intense yellow solution, from which was isolated 9,10-dihydroazepino[1,2-*a*]indol-8-one (**29**), identical in m.p. and spectra with that previously reported[2] (variable yield). The next compound eluted was 2-methoxyacridan (**30**), m.p. 132–134 °C (lit.,[15] m.p. 133.5–136 °C) (0.05 g, <2%); δ_H 3.7 (3 H, s), 4.0 (2 H, s), 5.9 (1 H, br s, NH) and 6.3–7.9 (7 H, m). A mixed m.p. with a synthetic specimen showed no depression. The fifth compound was the amine **2d** (0.775 g, 29%) and the sixth 2-methoxyacridine (**31**) m.p. 89–91 °C (lit.,[20] m.p. 89–91 °C) (0.131 g, 5%); δ_H 3.85 (3 H, s), 6.9–8.1 (7 H, m) and 8.35 (1 H, s, 9-H).

2-*Azido*-5-*methoxydiphenylmethane* (**10**).—The azide **10** (0.4 g) gave the *azepinoindole* **26**, m.p. 93 °C [light petroleum (b.p. 60–80 °C)], eluted with light petroleum (b.p. 60–80 °C) (0.06 g, 17%) (Found: C, 79.35; H, 6.4; N, 6.55. $C_{14}H_{13}NO$ requires 79.6; H, 6.2; N, 6.65%); *m*/*z* 211 (M$^+$, 100%), 210 (25), 168 (63) and 167 (35); δ_H 3.3 (2 H, d, 10-, 10′-H), 3.7 (3 H, s), 5.4–5.9 (4 H, m, 7-, 8-, 9-, 11-H) and 6.5–7.2 (4 H, m, 1-, 3-, 4-, 6-H). Elution with ethyl acetate gave the amine **9** (0.116 g, 32.5%).

2-*Azido*-4′-*nitrodiphenylmethane* (**15**).—The azide (1.92 g) gave a crude mixture of four products. Only one could be obtained pure by Chromatron separation, eluting with ethyl acetate. This compound was identified as azepino[1,2-*a*]indol-8-one (**32**), m.p. 128 °C (0.324 g, 22%), by comparison with a previously isolated sample,[2] δ_H 5.8 (1 H, dd, 9-H, *J* = 12 and 3

Hz), 6.25 (1 H, dd, 7-H, J = 12 and 3 Hz), 6.9 (1 H, s, 11-H) and 7.0–7.8 (6 H, m).

Acknowledgements

Linear least-squares analysis of the data was done using plotting routines supplied by Dr. P. Borrell.

One of us (B. D. L.) thanks the University of Keele for a grant.

References

1 Part 8. M. G. Hicks, G. Jones and D. C. York, *J. Chem. Soc., Perkin Trans. 1*, 1988, 69.
2 G. R. Cliff and G. Jones, *J. Chem. Soc. C*, 1971, 3418.
3 R. N. Carde and G. Jones, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2066.
4 R. N. Carde, G. Jones, W. H. McKinley and C. Price, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1211.
5 R. N. Carde, P. C. Hayes, G. Jones and C. J. Cliff, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1132.
6 L. O. Krbechek and H. Takimoto, *J. Org. Chem.*, 1968, **33**, 4286.
7 P. C. Hayes and G. Jones, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1871.
8 P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, 1962, **84**, 480.
9 A. Reiser, G. Bowes and R. J. Horne, *Trans. Faraday Soc.*, 1966, **62**, 3162.
10 J. M. Lindley, I. M. McRobbie, O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2194; C. Wentrup, ed., *Reactive Molecules*, Wiley, New York, 1984, pp. 182–185.
11 E. F. V. Scriven and K. Turnbull, *Chem. Rev.*, 1988, **88**, 221.
12 L. K. Dyall, *Aust. J. Chem.*, 1975, **28**, 2147.
13 M. P. Thorne, *Can. J. Chem.*, 1967, **45**, 2537; E. A. Jordan and M. P. Thorne, *J. Chem. Soc., Perkin Trans. 2*, 1984, 647.
14 M. Lamchen and A. J. Wicken, *J. Chem. Soc.*, 1959, 2779.
15 J. F. J. Dippy and V. Moss, *J. Chem. Soc.*, 1952, 2205.
16 B. Staskun, *J. Am. Chem. Soc.*, 1964, **86**, 2856.
17 R. E. Davies, H. T. Openshaw, F. S. Spring, R. H. Stanley and A. R. Todd, *J. Chem. Soc.*, 1937, 1119.
18 R. B. Moodie, P. N. Thomas and K. N. Schofield, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1693.
19 G. R. Cliff and G. Jones, *J. Chem. Soc. C*, 1976, 1490.
20 A. K. Colter, P. Plank, J. P. Bergsma, R. Lahti, A. A. Quesnel and A. G. Parson, *Can. J. Chem.*, 1984, **62**, 1780.
21 T. Hudlicky, T. M. Kitchen and S. M. Naqvi, *Org. React.*, 1985, **33**, 247.
22 L. K. Dyall, *Aust. J. Chem.*, 1986, **39**, 89.
23 R. K. Smalley and H. Suschitzky, *J. Chem. Soc.*, 1963, 5571; R. K. Smalley, W. A. Strachan and H. Suschitzky, *Tetrahedron Lett.*, 1974, 825.
24 P. W. Atkins, *Physical Chemistry*, 2nd edn., Oxford University Press, Oxford, 1982, p. 940.
25 Fuji Photo Co. Ltd, *Jpn. Kokai Tokkyo Koho JP* 60, 112, 483 [85, 112, 483] 18th June 1985 (*Chem. Abstr.*, 1985, **104**, 43227).
26 E. J. Engels, M. Lamchen and A. J. Wicken, *J. Chem. Soc.*, 1959, 2694.
27 P. G. Gassman and H. R. Drewes, *J. Am. Chem. Soc.*, 1978, **100**, 7600; *J. Chem. Soc., Chem. Commun.*, 1973, 488.
28 C. L. Hewett, L. J. Lermit, H. T. Openshaw, A. R. Todd, A. H. Williams and F. N. Woodward, *J. Chem. Soc.*, 1948, 292.

Paper 1/05827D
Received 18*th November* 1991
Accepted 14*th February* 1992