Competitive Cyclisations of Singlet and Triplet Nitrenes. Part 8.[1] The 1-(2-Nitrenophenyl)pyrazoles and Related Systems

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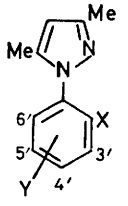
The title nitrenes, derived by nitro-group deoxygenation with triethyl phosphite or by thermolysis or photolysis of the corresponding azide, have been studied. The effect of substituents (Cl, Br, OMe, NMe_2, Me, CF_3, and NO_2) both *meta* and *para* to the nitrene has been examined as a determinant of the preferred mode of cyclisation to either a pyrazolobenzotriazole or a pyrazoloquinoxaline. Similarly, the role of solvents, sensitisers, and quenchers has been studied. Routes to the isomeric 1- and 2-(2-nitrophenyl)-4,5,6,7-tetrahydroindazoles have been defined and the literature corrected by studying the nitrene-mediated cyclisation of these products. The chemistry of the analogous 1-(2-carbenophenyl)- and the 1-(2-nitrenosulphonylphenyl)-3,5-dimethylpyrazoles has also been examined, the former giving 2-(3,5-dimethylpyrazol-1-yl)-benzaldazine and -benzyl alcohol while the latter gave products of intramolecular nitrene attack (a pyrazolobenzothiatriazine) and intermolecular reaction. Rationalisations for all the reaction pathways have been advanced.

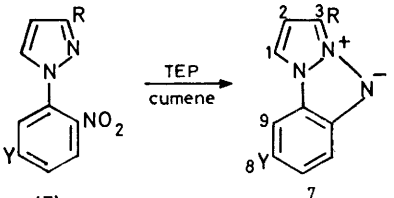
In a preliminary communication [2] we examined the reactions of 1-(2-nitrenophenyl)-3,5-dimethylpyrazoles (1) as the archetype of compounds having an attractive site for attack by the singlet (2-N) or triplet (pyrazole 5-Me) nitrene species. We herein report the full details



(1) X = N
(2) X = NO_2
(3) X = NH_2
(4) X = N_3

of this work and apply the results to the solution of a puzzling structural problem.

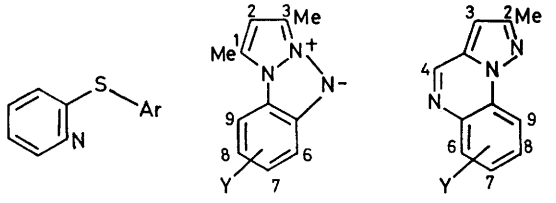
In 1965, Lynch and Hung [3] reported that deoxygenation of 2-nitrophenylpyrazole (5a) with triethyl phosphite (TEP) gave the pyrazolobenzotriazole (6a) in 18% yield. We considered that if this were a singlet-nitrene-mediated reaction, increasing the eletrophilicity of the nitrene [with, for example, a *p*-chloro-substituent, *e.g.* (5b and d)] or the nucleophilicity of the pyrazole 2-nitrogen atom [with a 3-methyl group *e.g.* (5c and d)] should improve product yields. This was indeed borne out (Scheme 1) particularly when the two effects are combined. We have found this to be an important principle throughout our nitrene work, optimum yields of singlet nitrene products being obtained by appropriate substitution of the substrate. Thus with 2-nitrenophenyl phenyl sulphides (7; Ar = Ph) [4] and the analogous thiophens (7; Ar = 2-thienyl) [5] and benzothiophens (7; Ar = 2-benzothienyl),[1] the presence of methyl groups in the attacked ring [Ar in (7)] and a chloro-



(5) (6) (7)

Yield of (6) (%)	
a; Y = R = H	15
b; Y = Cl, R = H	21
c; Y = H, R = Me	29
d; Y = Cl, R = Me	65

SCHEME 1



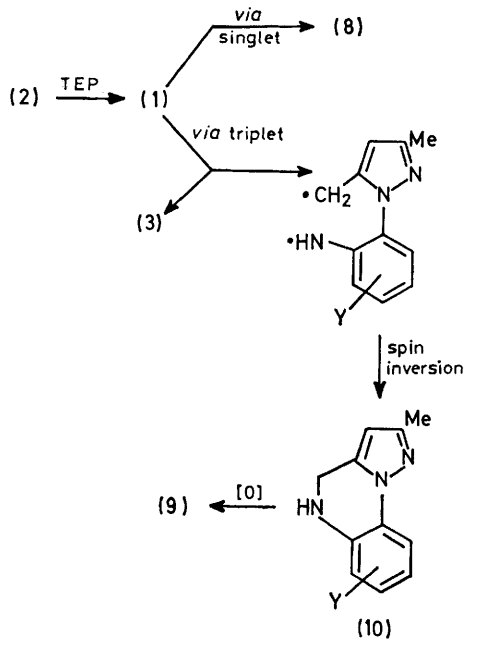
(7) (8) (9)

substituent *para* to the nitrene have a dramatic effect on product yields. We therefore chose the 3,5-dimethylpyrazole (1) for our studies, using the *p*-chloro-derivative (1; Y = 5′-Cl) by choice.

In order to verify the role of the substituent in the benzenoid ring we deoxygenated a series of nitrophenylpyrazoles (2) with a variety of substituents both *para* (2; 5′-Y) and *meta* (2; 4′-Y) to the incipient nitrene. Three types of products were formed: the pyrazolobenzotriazoles (8) which we have argued derived from the singlet nitrene; and the pyrazoloquinoxalines (9) and the aminophenylpyrazoles (3), derivable by intra- and inter-molecular hydrogen atom abstraction respectively by the triplet nitrene, followed in the former case by radical recombination and oxidation (Scheme 2). This view is supported by the conversion of the amine (3; Y = 5′-Cl) into the pyrazoloquinoxaline (9; Y = 8-Cl) by oxidation with active manganese dioxide, a process known to involve radical coupling.[6] All our work suggests that some of the amine formation derives from dehydrogenation of the dihydro-species [*e.g.* (10)]

by the triplet nitrene.[7] The results are summarised in Table 1 and reveal some significant trends.

While electron-withdrawing groups *para* to the nitrene indeed enhance singlet product (8) yields, only triplet-derived products (9) and (3) result when *p*-NMe_2 and *p*-OMe substituents are employed. Clearly the singlet



SCHEME 2

nitrene is totally deactivated under these conditions and undergoes spin-inversion to yield the lower-energy triplet state. This phenomenon accounts for the high yields of azo-compounds (again, triplet derived) from the decomposition of *p*-methoxyphenyl azide [8] and offers an excellent thermal route to exclusive triplet nitrene-derived products that we have made good use of elsewhere.[9] The effect of substituents *meta* to the nitrene

TABLE 1

Products from deoxygenation of 1-(2-nitrophenyl)-3,5-dimethylpyrazoles (2) with TEP

	Products (%) *		
Y	(8)	(9)	(3)
H	6	t	5
5′-Cl	62	16	11
5′-Br	70	6	2
5′-NMe_2	0	47	19
5′-OMe	0	23	32
4′-Cl	57	0	t
4′-CF_3	63	0	t
4′-NO_2	26	0	t
4′-Me	63	0	t

* t = Trace.

is less easily rationalised. Clearly, only an inductive effect will influence the nitrene electrophilicity. However, a group which increases the electrophilicity of the nitrene will decrease the nucleophilicity of the pyrazole and *vice versa*. Albeit the results indicate that both kinds of substituents enhance the singlet pathway almost to the exclusion of any triplet product formation.

The question of nitrene participation in nitro-compound deoxygenation with TEP is still an argued issue. In order to obviate concerted or other routes to the products (8) and (9) we have conducted several checks and report also the thermal and photodecomposition of the corresponding azides (4). Firstly, neither the dipolar pyrazolobenzotriazoles (8) nor the phosphorimidate [1; X = N:P(OEt)$_3$ instead of N; Y = 5′-Cl) are changed under the reaction conditions, and the nitro-compound (2; Y = 5′-Cl) is unchanged on heating in an inert solvent. Nitrene reactions are known to be sensitive to solvent effects. Thus, singlet ⟶ triplet interconversion is assisted by use of solvent containing a heavy atom through collisional deactivation.[7] When the nitrophenylpyrazole (2; Y = 5′-Cl) was deoxygenated with hot TEP in either TEP, cumene, or bromobenzene solutions the results in Table 2 were obtained,

TABLE 2

Deoxygenation of 1-(5-chloro-2-nitrophenyl)-3,5-dimethylpyrazole (2) in various solvents

	Products (%)			
Solvent	(8)	(9)	(3)	*S*/*T* *
TEP	66	0	3	22
Cumene	62	16	11	2.3
PhBr	50	14	3	2.9

* *S*/*T* indicates the ratio of singlet to triplet products.

which although they indicate that the use of neat TEP is the most effective synthetic procedure (in contradistinction to the literature indications [10]) they shed little light on the reaction mechanism. Since several steps supervene the nitrene formation and reaction which could be solvent-dependent we made a careful study of the corresponding azide (4) decompositions.

The effect of solvents on the thermolysis of the azide (4; Y = 5′-Cl) is shown in Table 3. Several interesting

TABLE 3

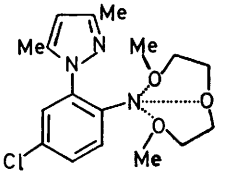
Solvent effects on the thermolysis of the 1-(2-azido-5-chlorophenyl)-3,5-dimethylpyrazoles (4; Y = 5′-Cl)

		Temp.	Products (%) *			
Expt.	Solvent	(°C)	(8)	(9)	(3)	*S*/*T*
1	Decalin	192	55	6	t	9.2
2	Decalin	152	32	8	5	2.5
3	Cumene	152	39	5	2	5.6
4	Cumene–O_2	152	0	t	0	
5	Diglyme	162	t	8.5	83.5	0.1
6	Bromobenzene	155	8	6	21	0.3
7	Dimethyl sulphoxide	160	36	7	8	2.4
8	Dimethyl sulphoxide–Cu	160	t	26	41	v. low

* t = Trace.

points emerge. First, as we have noted elsewhere,[7,11] thermally excited singlet nitrenes react much faster, giving fewer triplet by-products (Experiments 1 and 2) and higher yields. By contrast, any solvents or adducts which interact strongly with the singlet species thus stabilising and deactivating it cause higher triplet-derived product yields. Thus, diglyme would appear to so deactivate the singlet species by lone-pair interaction (11) as to allow singlet ⟶ triplet interconversion rather than reaction at N. The derived triplet nitrene finds a rich supply of abstractable hydrogen at near bonding distance, thus giving mostly the amine (3) (83.5%).

The much weaker interaction of two pairs of lone-pair electrons, resulting in singlet nitrene lifetime extension, (and thus *increased* yields of singlet-derived products) has been the subject of theoretical [12] and experimental study using both dichloromethane [7,13] and more recently dioxan.[14] A similar effect of copper yielding an unreactive singlet nitrene–copper complex [15] (a ' nitrenoid ') could account for the higher triplet yields in experiment 8, while the ' heavy atom effect ', already mentioned is noted in experiment 6. Oxygen, a triplet quencher, is evidently disastrous in these reactions



(11)

(experiment 4) as is further borne out in later kinetic studies. All our other reactions were purged with nitrogen to avoid such problems. Indeed, the pyrazolobenzotriazoles decompose under these reaction conditions, as indicated by a blank experiment. That nitrenes were involved in these processes (as opposed to a concerted cyclisation with loss of nitrogen, for example) was demonstrated in two ways. First, all the azides decomposed above 140°. Secondly, a kinetic study of the decomposition of 1-(2-azido-5-chlorophenyl)-3,5-dimethylpyrazole (4; Y = 5'-Cl) in both diglyme and in cumene at 152° under identical conditions was undertaken. The solvents were freshly distilled from lithium aluminium hydride to remove peroxide material.* First-order kinetics with almost identical rate constants [k (diglyme) 4.5×10^{-4}, k (cumene) 4.1×10^{-4} s^{-1}] were

TABLE 4

The thermolysis of various 1-(2-azidophenyl)-3,5-dimethylpyrazoles (4)

Expt.	Y	Solvent	Expt. (°C)	Products (%) (8)	(9)	(3)	S/T
1	5'-Cl	Cumene	152	39	5	2	5.6
2	5'-Br	Cumene	152	26	11	11	1.2
3	5'-Br	Bromobenzene	154	4	8	2	0.4
4	5'-NMe_2	Cumene	152	0	44	40.5	v. low
5	5'-NMe_2	Diphenyl ether	240	0	60	18	v. low
6	4'-CF_3	Decalin	189	67	0	0	v. high
7	4'-CF_3	Diglyme	160	42	t	16.5	2.5

obtained. These results, which indicate that reactions leading to the pyrazolobentriazole (8) and the amine (4) proceed at the same rate strongly support a nitrene intermediate.

The role of substituents was again briefly checked and the results are collected in Table 4. The results broadly agree with the trends already noted, although from a synthetic viewpoint deoxygenation appears a better method for making the nitrenophenylpyrazoles. The ' diglyme effect ' (experiment 7) is again evident though it is less marked than in the earlier example. Also, the powerful effect of thermal excitation leading to increased product yields both from singlet (see experiments 6 and 7) and triplet (see experiment 4 and 5) nitrenes is again seen.

We have further examined the photolysis of the same azides as a function of solvent, then of temperature and also of substituent and solvent (Table 5).

Some facts deserve further comment. First, efficient formation of the singlet-derived product (8) clearly requires a thermally derived nitrene. The generally low overall yields on photolysis under ' singlet-promoting ' conditions are probably due to the photoinstability

TABLE 5

The photolysis of various 1-(2-azidophenyl)-3,5-dimethylpyrazoles (4)

Y	Solvent	Products (%) (8)	(9)	(3)	S/T
5'-Cl	C_6H_6	18	t	8	2.25
5'-Cl	CH_2Cl_2	28	6	1	4
5'-Cl	CH_2Cl_2–pyrene	42	3	t	14
5'-Cl	Me_2SO	21	t	48	0.4
5'-Cl	PhAc	0	48	42.5	v. low
5'-Cl	Petroleum at 107°	10	14.5	11.5	0.4
5'-Cl	PhAc–PhCl (1 : 9) at 107°	0	22	34	v. low
5'-Br	CH_2Cl_2	t	21	24	v. low
5'-Br	CH_2Cl_2–pyrene	10	9	14.5	0.4
5'-Br	PhAc	0	22.5	11	v. low
4'-CF_3	CH_2Cl_2	33	0	13	2.5
4'-CF_3	CH_2Cl_2–pyrene	15	0	44	0.3
4'-CF_3	PhAc	0	41	22	v. low
5'-NMe_2	CH_2Cl_2	0	11.5	18.5	v. low
5'-NMe_2	CH_2Cl_2–pyrene	0	8	15	v. low
5'-NMe_2	PhAc	0	50	38	v. low

of the pyrazolobenzotriazoles (8). Photolyses at 107° also gave poor overall yields.

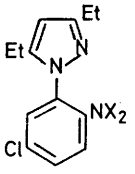
Pyrene is a well-known triplet quencher and singlet photosensitiser [17] and its presence has a marked effect on the singlet–triplet balance. The beneficial role of methylene chloride for optimising singlet pathways has already been noted.

One surprising feature throughout this work is the complete absence of azo-compound formation. We have noted elsewhere that this reaction is the last resort of an unreactive triplet nitrene and is especially evident during acetophenone-sensitised photolyses.[7,11] Clearly intramolecular hydrogen-atom abstraction from the 5-methyl group of the pyrazole is a low-energy process. Only in the absence of the 3,5-dimethyl groups is azo-compound formation noted. Thus 1-(5-chloro-2-azidophenyl)pyrazole on photolysis in acetophenone gave 4,4'-dichloro-2,2'-dipyrazol-1-ylazobenzene (35%). Higher overall yields of triplet products are readily achieved by ambient temperature photolyses in acetophenone, even in those cases where thermolysis gave only singlet products. Thus the 4-trifluoromethyl azide (4; Y = 4'-CF_3) gave only the pyrazolobenzotriazole (8) (67%) on thermolysis in decalin but on photolysis in acetophenone gave solely the pyrazoloquinoxaline (9) (41%), a useful synthetic dichotomy. The powerful

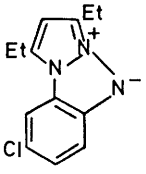
* Without this safeguard, S–shaped kinetic plots suggestive of autocatalysis by peroxides were observed (*cf.* ref. 16).

influence of a dimethylamino-group *para* to the azide leading only to triplet products on thermolysis is also observed on photolysis irrespective of the solvent, though acetophenone gives the best yields. This we attribute to the fact that *all* the light is absorbed by the solvent, preventing secondary photodecompositions.

Having established some general principles in these



(12) X = O
(13) X = N
(14) X = H



(15)

(16)

nitrene pathways, we next extended them to other 5-alkyl analogues of pyrazoles. Triplet nitrenes are noted for their ability to dehydrogenate longer alkyl side-chains, possibly by abstraction of two hydrogen atoms concertedly.[18] We thus examined the 3,5-diethylpyrazoles (12) and (13). A similar pattern of products

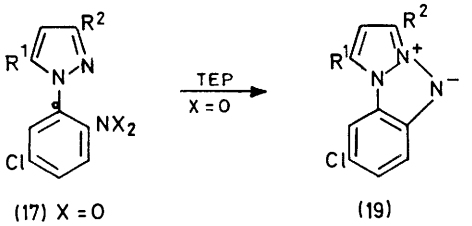
TABLE 6

Products from decomposition of the pyrazoles (12) and (13)

Compound	Conditions	Products (%) (15)	(16)	(14)
(12)	TEP–cumene	44	2	2
(13)	Heat–cumene	39	2.5	2
(13)	*hν*–PhAc	0	39	22

to the above were observed (Table 6) with no evidence of other pathways. Once more the two types of cyclisation product (15) and (16) could be almost exclusively synthesised by proper choice of conditions.

The possibility of the nitrene attacking other than pyrazole 5-alkyl groups was finally considered. The



(17) X = O
(18) X = H

(19)

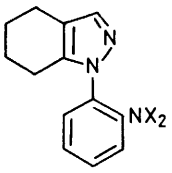
a: R^1 = OH, R^2 = Me
b: R^1 = NHAc, R^2 = Me
c: R^1 = R^2 = Ph

Yield (%) (18)	(19)
0	0
8	5
56	15

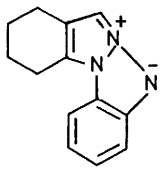
SCHEME 3

5-hydroxy, 5-acetylamino, and 5-phenyl derivatives (17) were subjected to deoxygenation (Scheme 3) with no evidence of attack on the 5-substituent.

During the course of our work Tsuge and Samura [19] reported that the deoxygenation of 1-(2-nitrophenyl)-tetrahydroindazole (20), gave the indazolobenzotriazole (23). This claim seemed doubtful because of the ambiguous synthesis of the starting material, made by treatment of tetrahydroindazole with 2-nitrochlorobenzene in the presence of potassium acetate and copper(II) acetate at 210—220° for 24 h. Since two isomers are possible, (20) and (24), we made a careful study of several routes



(20) X = O
(21) X = N
(22) X = H



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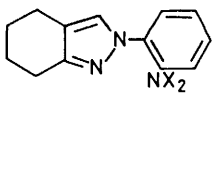


(24) X = O
(25) X = N
(26) X = H

to the nitrophenylindazoles (20) and (24) examining the products by h.p.l.c. (both analytically and preparatively), and subjected the products to nitrene-mediated decompositions. This enabled us to define unambiguously the structures of the nitrophenylindazoles tabulated in Table 7, as shown in the sequel. The method employed by the Japanese workers, in our hands gave much tar and very low yields producing only the 2-isomer and not the 1-isomer as proposed by Tsuge and Samura. The best routes to the 1-isomer are methods 2 and 6.

Use of the silver salt of tetrahydroindazole gave almost equal amounts of the two isomers while the bulkier thallium(I) salt, surprisingly, favoured the 1-isomer. While the isomers are not easily separated by crystallisation or chromatography, the mixed products of deoxygenation are readily resolved. Deoxygenation of

TABLE 7

Routes to the nitrophenylindazoles (20) and (24)

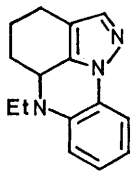
Method Reagents *	Temp. (°C)	Time (h)	Product yields (%) Overall	(20)	(24)
1 THI, ONCB, KOAc, $Cu(OAc)_2$, N_2 [20]	210—220	24	4	0	100
2 THI, ONFB, KF [21]	120—130	24	32	94	6
3 THI, ONBB, K_2CO_3, $CuBr_2$, $PhNO_2$ [22]	Reflux	24	0	0	0
4 THI–Ag, ONFB, KF	120—130	24	90	53	47
5 THI–Tl, ONFB, KF	120—130	24	91	65	35
6 ONPH,HCl, 2-HMC, EtOH	Reflux	4	94	94	6

* THI is 4,5,6,7-tetrahydroindazole; THI–Ag and THI–Tl are the corresponding silver and thallium salts of THI; ONCB, ONFB, and ONBB are *o*-nitro-chloro-, -fluoro-, and -bromobenzenes, respectively; ONPH is *o*-nitrophenylhydrazine; 2-HMC is 2-hydroxymethylenecyclohexanone.

the two isomeric nitrophenylindazoles is very illuminating. The 1-isomer (20) gave no indazolobenzotriazole (23) [similarly not formed from the azide (21) on thermolysis or photolysis] but a good yield (50%) of the indazoloquinoxaline (27). The ethyl group probably derives from triethyl phosphate alkylation of the intermediate dihydroquinoxaline. The 2-isomer (24) on the other hand gave (as noted by Tsuge and Samura but erroneously attributed to the 1-isomer) the indazolobenzo-

triazole (28) in 19% yield. Surprisingly the 1-(2-azidophenyl)tetrahydroindazole (21) proved unproductive on both thermolysis or photolysis giving solely the amine (21) admixed with the corresponding azo-compound.

The competitive intramolecular reactions of singlet and *triplet nitrenes* are conveniently observed with 1-(2-nitrenophenyl)-3,5-dimethylpyrazoles. We, therefore, considered this system as a possible structure to observe competing pathways in the carbene (29) and sulphonylnitrene (30) analogues. To this end we examined the



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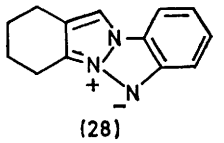
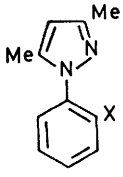
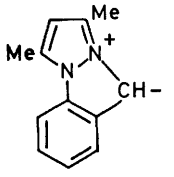


(28)

decomposition of the *p*-tolylsulphonylhydrazide (31), the diazomethane (32), and the sulphonyl azide (33).

The carbene precursors (31) and (32) were conveniently synthesised as shown in Scheme 4, by metallation of 1-phenyl-3,5-dimethylpyrazole (37). The aldehyde (38) was readily converted into the tosylhydrazone (31) and hydrazone (39) by standard methods. Attempts to generate the diazomethane (32) from the tosylhydrazone (31) by Farnum's method [23] gave poor yields, as did oxidation of the unstable hydrazone (39) with yellow



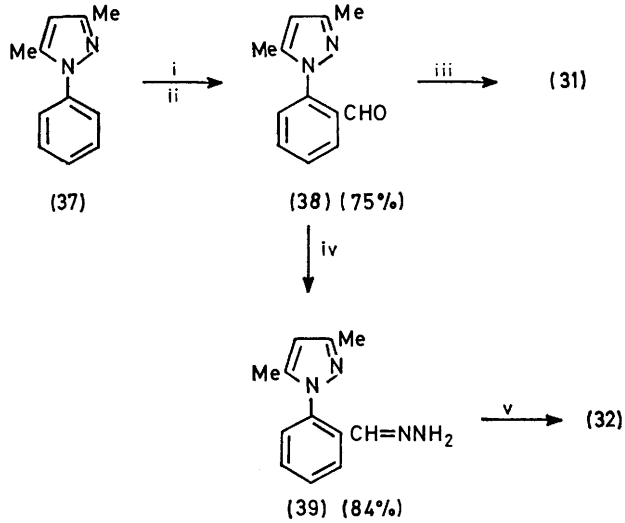


(40)

(29) X = CH
(30) X = SO_2N
(31) X = CH:NNHSO$_2$C$_6$H$_4$Me-*p*
(32) X = CHN_2
(33) X = SO_2N_3
(34) X = (CH:N–)$_2$
(35) X = CH_2OH
(36) X = SO_3H

mercury(II) oxide, known to be erratic.[24] However, efficient oxidation occurred with silver(I) oxide.[24]

Decomposition of both the carbene precursors showed no intramolecular reaction products. The tosylhydrazone (31) with sodium methoxide in diglyme [25] gave a mixture of the azine (34) (46%) and the benzyl alcohol (35) (10%). The former well known type of product probably derives from attack of one diazomethane (32) moiety by its terminal nitrogen [26] on the carbene (29), though other mechanisms have been noted.[27] Benzyl alcohol formation has been observed before from carbenes [28] and rationalised either by the action of adventitious water or (less likely in this case) by protonation of the carbene to a carbonium ion and subsequent reaction.[29] In our case such a cation would almost certainly prefer attack at the pyrazole 2-N. However, the possible intermediacy of the ylide (40) is an attractive

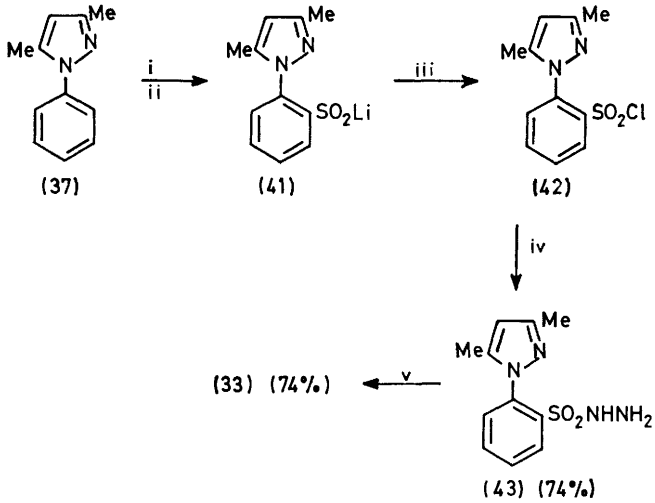


SCHEME 4 Reagents: i, BuLi; ii, DMF; iii, *p*-MeC$_6$H$_4$SO$_2$NHNH$_2$; iv, NH_2NH_2; v, Ag_2O

alternative which could account for the surprising lack of intramolecular reaction products.

Thermolysis or photolysis of the diazomethane resulted in formation of the same azine (34), the irradiation only being effective through a quartz filter. The structure of both the azine (34) and the benzyl alcohol were confirmed by unambiguous synthesis.

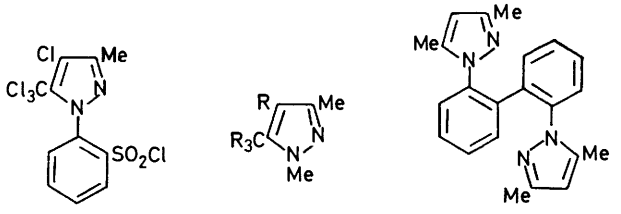
Attempts to prepare the sulphonyl azide (33) by condensation of sodium 2-chloro-5-nitrobenzenesulphonate



SCHEME 5 Reagents: i, BuLi–0°; ii, SO_2; iii, MeCONHCl; iv, NH_2NH_2; v, HNO_2

with 3,5-dimethylpyrazole (analogous to our successful synthesis of other related heterocycles [30]) even under melt conditions were unproductive. We, therefore, followed a pathway related to that for the carbene precursors as outlined in Scheme 5. The metallated 1-phenyl-3,5-

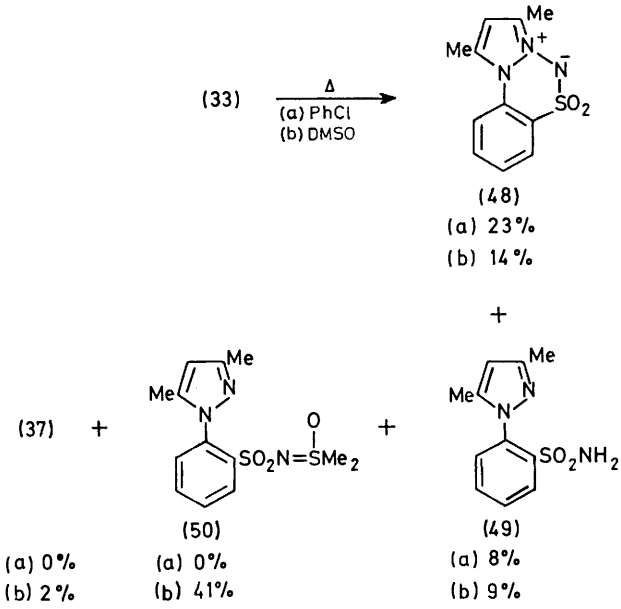
dimethylpyrazole (37) was treated with sulphur dioxide and the resulting lithium sulphinate (41) treated *in situ* with *N*-chloroacetamide. Scott and his co-workers have converted sulphinates into sulphonyl chlorides using chlorine.[31] However, in our case chlorine in excess gives a pentachlorinated derivative (44) by analogy with the known ready chlorination of other 3,5-dimethylpyrazoles [32,33] (45) ⟶ (46). Molar amounts of chlorine in carbon tetrachloride gave mixtures of



(44) (45) R = H (46) R = Cl (47)

chlorinated products. *N*-Chloroacetamide proved ideal being a soluble and efficient chlorinating agent, unlike the lesser soluble *N*-chlorosuccinimide. Attempts to form the sulphonyl azide directly from the sulphonyl chloride with sodium azide in ethanol led surprisingly to the sulphonic acid (36) admixed with the 2,2′-bis-(3,5-dimethylpyrazol-1-yl)biphenyl (47). Hence the indirect route shown in Scheme 5 was employed, the overall procedure requiring only two isolations, the hydrazide (43) and the azide (33).

The sulphonyl azide (33) was decomposed in two



SCHEME 6

different solvents, chlorobenzene and dimethyl sulphoxide (DMSO) following, surprisingly, two distinct pathways (Scheme 6). In both cases the expected singlet-derived pyrazolobenzothiatriazine dioxide (48) was isolated though not in high yield. This is another rare example of formation of an unfavoured six-membered ring *via* a nitrene.[34] The major singlet pathway in DMSO was the intermolecularly trapped sulphoximide (50) by analogy with the well documented reaction of benzenesulphonyl azides.[8] The two other products (49) and (37), both formed in very low yield, are triplet derived and follow existing patterns of reactivity.[30,35] Despite the known propensity of sulphonyl nitrenes to attack benzylic methyl groups [34] no such reaction was observed in the present case, even though seven-membered ring formation is known from a sulphonyl nitrene.[34]

EXPERIMENTAL

The general condition were as specified in Part 4.[4] Photolyses were conducted in an immersion system using a 125 W medium pressure lamp and a Pyrex filter, employing 1% solutions. H.p.l.c. utilised a Waters Associates ALC 202 instrument. Petroleum refers to b.p. 60—80° while light petroleum refers to b.p. 40—60°. ^{13}C N.m.r. off-resonance multiplicities follow the chemical shifts.

Preparation of the 1-(2-*Nitrophenyl*)*pyrazoles*.—(i) 3,4-*Dinitrohalogenobenzenes*. Fuming nitric acid (120 ml) was added to concentrated sulphuric acid (98%; 150 ml) with ice cooling. The *m*-halogenonitrobenzene (25 g) was added over 15 min to the above mixture keeping the temperature below 30°, and with constant stirring. After 1 h the solution was poured onto ice and the resulting solid filtered off, washed well with water, aqueous sodium carbonate, and again water, and dried in a vacuum desiccator over phosphorus pentaoxide. In this way was obtained the fluoro- (80%), m.p. 54—56° (lit.,[36] 55—56°), chloro- (97%), m.p. 40° (lit.,[37] 40.5°), and bromo-3,4-dinitrobenzene (94%), m.p. 58—59° (lit.,[38] 59—60°).

(ii) 2-*Nitrophenylhydrazines*.—(a) A mixture of the 3,4-dinitrohalogenobenzene (5.0 g) and urea (2 g) was dissolved in ethanol (50 ml). To this solution was added hydrazine hydrate (2 g) and the solution allowed to stand overnight. The precipitate was filtered off and recrystallised from ethanol to give 5-chloro-2-nitrophenylhydrazine (76%), m.p. 165°, (lit.,[39] 164°) and 5-bromo-2-nitrophenylhydrazine, m.p. 163° (lit.,[39] 162°).

(b) 4-Methyl-2-nitroaniline (20.0 g) was dissolved in hot concentrated hydrochloric acid (50 ml) and water (50 ml). The solution was rapidly cooled to 0° and diazotised with sodium nitrite (8.8 g) in water (40 ml). The diazotised solution was filtered through a plug of glass wool and added slowly with stirring to an ice-cold solution of tin(II) chloride (70 g) in concentrated hydrochloric acid (70 ml). The yellow precipitate that formed was filtered off and added to a saturated solution of sodium acetate (200 ml), and the resulting orange solid extracted thoroughly with ether. Evaporation of the dried ($MgSO_4$) extract gave 4-methyl-2-nitrophenylhydrazine as orange crystals (14.0 g, 64%) from ethanol, m.p. 109—111° (lit.,[40] 110°). In the same manner, 4-chloro-2-nitroaniline was converted into 4-chloro-2-nitrophenylhydrazine (78%), m.p. 134° (lit.,[41] 134°).

(c) A mixture of 2-chloro-5-trifluoromethylnitrobenzene (2.25 g), hydrazine hydrate (0.5 g), and sodium carbonate (1 g) was suspended in dimethylformamide (50 ml), when the colour turned to dark orange and heat was evolved. Finally, the solution was heated on a water-bath for 1 h and poured into water (250 ml). The precipitate was filtered and recrystallised from ethanol giving 2-*nitro*-4-*trifluoromethylphenylhydrazine* (1.6 g, 72%) as orange needles, m.p. 116—117° (Found: C, 38.3; H, 3.05; N, 19.3.

$C_7H_6F_3N_3O_2$ requires C, 38.0; H, 2.7; N, 19.0%); $\nu_{max.}$ (Nujol) 3 340 and 3 100 cm^{-1} ($NHNH_2$); δ($CDCl_3$) 9.25br (1 H, s, NH), 7.54—8.53 (3 H, m, aromatic), and 3.67br (2 H, s, NH_2).

(iii) (a) Dipropionylmethane [42] was synthesised by a literature method. Acetoacetaldehyde dimethyl acetal, *dibenzoylmethane*, and malonaldehyde tetramethyl acetal were purchased (Aldrich). The appropriate 2-nitrophenylhydrazine (0.01M) was dissolved in ethanol (20 ml) containing concentrated sulphuric acid (98%, 3 ml) and to this solution was added the requisite β-dicarbonyl compound (0.01M) in acetic acid (3 ml). The mixture was refluxed for 4—6 h and poured into water, and the products filtered off or extracted. Purification by recrystallisation or column chromatography on alumina gave the pyrazoles recorded in Table 8.

(b) 3,5-Dimethylpyrazole (9.6 g, 0.01M), *o*-fluoronitrobenzene (14.0 g, 0.1M), and anhydrous potassium fluoride (7 g) were heated together with stirring at 120—140° for 12 h. The cooled reaction mixture was extracted thoroughly with chloroform and the extract evaporated. The off-white solid was recrystallised from petroleum (b.p. 80—100°) to afford 1-(2-nitrophenyl)-3,5-dimethylpyrazole as crystals (18.6 g, 86%), m.p. 106—107° (lit.,[43] 102°).

(c) 1-(5-Bromo- or 5-chloro-2-nitrophenyl)-3,5-dimethylpyrazole (0.1M), dimethylamine hydrochloride (0.15M) in water (5 ml), and sodium hydrogencarbonate (2 g) in pyridine (50 ml) were heated together overnight under reflux. The mixture was poured into water and the yellow precipitate filtered off, washed, dried, and recrystallised from ethyl acetate to give 1-(5-*dimethylamino*-2-*nitrophenyl*)-3,5-*dimethylpyrazole* (2; Y = 5′-NMe_2) (96%), m.p. 177—178°.

(d) A solution of 1-(5-chloro-2-nitrophenyl)-3,5-dimethylpyrazole (12.5 g) in ethanol (100 ml) containing potassium hydroxide (2.8 g) was kept at 60° for 140 h. The mixture was concentrated and diluted with water (200 ml) to give a brown solid which was filtered off, washed, dried, and recrystallised from petroleum to give 1-(5-*methoxy*-2-*nitrophenyl*)-3,5-*dimethylpyrazole* (2; Y = 5′-OMe) as pale yellow needles (12.0 g, 98%), m.p. 76—78°.

Data for the above pyrazoles are collected in Table 8.

(e) 1-(5-*Chloro*-2-*nitrophenyl*)-5-*hydroxy*-3-*methylpyrazole* (17a). A mixture of 5-chloro-2-nitrophenylhydrazine (9.3 g) and ethyl acetoacetate (6.5 g) were heated with stirring at 120° for 4 h. The orange solid obtained on cooling was recrystallised from petroleum (b.p. 100—120°) to give orange crystals of the hydrazone of ethyl acetoacetate (13.4 g, 90%), m.p. 121° (lit.,[46] 121°). This hydrazone (4.4 g) was heated in polyphosphoric acid (40 g) at 100° for 40 min with stirring and the solution poured into ice–water. The yellow precipitate was filtered off, washed with water, and recrystallised from ethanol as pale yellow crystals of the *title compound* (3.2 g, 91%), m.p. 172—174°. The i.r. spectrum in Nujol showed an OH absorption (3 500 cm^{-1}) but no carbonyl frequency. A solution spectrum (in chloroform) showed both an OH (3 500 cm^{-1}) and a carbonyl absorption (1 730 cm^{-1}).

(f) 5-*Acetamido*-1-(5-*chloro*-2-*nitrophenyl*)-3-*methylpyrazole* (17b). A mixture of 5-chloro-2-nitrophenylhydrazine (3.7 g), 3-aminocrotononitrile (85% pure, 2.0 g), and acetic acid (20 ml) was heated under reflux for 4 h. The mixture was poured into water and the orange precipitate filtered off, washed with water, and dried. Chromatography on alumina using diethyl ether as eluant gave 5-*amino*-1-(5-*chloro*-2-*nitrophenyl*)-3-*methylpyrazole* (2.0 g, 40%) which crystallised from ethanol, m.p. 160—162° (Found: C, 47.7; H, 3.6; N, 22.3. $C_{10}H_9ClN_4O_2$ requires C, 47.5; H, 3.6; N, 22.2%), $\nu_{max.}$ (Nujol) 3 400 and 3 200 cm^{-1}

TABLE 8

Properties of the 1-(2-nitrophenyl)pyrazoles (2), (5), (12), and (17)

Compound No.	Y	R¹	Yield (%)	M.p. (b.p./mmHg) (°C)	Lit. m.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	Chemical shift δ ($CDCl_3$) (*J*/Hz) Pyrazole ring	Benzene ring	Y	R¹	R²
(2)	H		86	106—107	102 [42]								2.14s and 2.19s (Me), 5.96s (4 H)	7.07—8.0m			
(2)	5′-F		29	98—99		56.1	4.3	18.1	$C_{11}H_{10}FN_3O_2$	56.2	4.25	17.9	2.14s and 2.20s (Me), 6.00s (4 H)	7.09—7.36m, 7.88—8.12m			
(2)	5′-Cl		74	106	106 [44]								2.19s and 2.23s (Me), 6.09s (4 H)	7.5—7.75m, 8.04d (3 H, *J* 9.0)			
(2)	5′-Br		68	111—112		44.2	3.7	14.5	$C_{11}H_{10}BrN_3O_2$	44.6	3.4	14.2	2.22s and 2.27s (Me), 6.09s (4 H)	7.65—8.07m			
(2)	5′-NMe_2		96	177—178		60.0	6.3	21.15	$C_{13}H_{16}N_4O_2$	60.0	6.2	21.5	2.21s and 2.28s (Me), 6.06s (4 H)	6.88dd (4 H, 6 H), 8.20d (3 H, *J* 9.0)	3.10s		
(2)	5′-OMe		98	76—78		58.4	5.5	17.3	$C_{12}H_{13}N_3O_3$	58.3	5.3	17.0	2.18s and 2.29s (Me), 5.97s (4 H)	6.9br, s (6 H), 7.07dd (4 H), 8.02d (3 H)	3.91s		
(2)	4′-Cl		75	129—131	129 [44]				$C_{12}H_{13}N_3O_3$				2.15s and 2.20s (Me), 6.05s (4 H)	7.4—8.14m			
(2)	4′-CF_3		85	119—121		50.2	3.7	15.0	$C_{12}H_{10}F_3N_3O_2$	50.5	3.5	14.7	2.16s and 2.22s (Me), 6.10s (4 H)	7.58—8.35m			
(2)	4′-NO_2		76	120	119—120 [44]								2.20s and 2.29s (Me), 6.14s (4 H)	7.77d (6 H, *J* 9.0) 8.47—8.9m			
(2)	4′-Me		51	103—105		62.0	5.5	18.1	$C_{12}H_{13}N_3O_2$	62.3	5.7	18.2					
(5a)	H	H	81	89	88—89 [45]								6.55t (4-H, *J* 2.5)	7.25—8.1m			
(5b)	5′Cl	H	97	58—59		48.1	2.5	19.0	$C_9H_6ClN_3O_2$	48.2	2.7	18.7	6.57t (4-H, *J* 2.0)	7.42—8.09m			
(5)	5′-NMe_2	H	86	139—141		56.8	5.2	24.0	$C_{11}H_{12}N_4O_2$	56.9	5.2	24.1	6.37t (4-H, *J* 2.5) 7.5—7.7m	6.44—6.67m, 7.90d (3-H, *J* 9.0)	3.05s		
(5c)	H	Me	64	(154/1) 48		59.2	4.6	20.6	$C_{10}H_9N_3O_2$	59.1	4.5	20.7	6.13d (4-H, *J* 2.5)	7.15—7.88m		2.20s	
(5d)	5′-Cl	Me	89	101—103		50.7	3.3	18.0	$C_{10}H_8ClN_3O_2$	50.5	3.4	17.7	6.23d (4-H, *J* 2.5)	7.32—7.99m		2.31s	
(12)			65	(136—138/0.35)		56.0	5.1	14.9	$C_{13}H_{14}ClN_3O_2$	55.8	5.0	15.0	1.15t (Me, *J* 8), 2.14—2.8m (CH_2), 5.94s (4 H)	6.85—7.9m			
(17a)		OH	91	172—174		45.2	2.6	17.8	$C_9H_6ClN_3O_3$	45.0	2.5	17.5	5.39s (4 H)	7.34—8.14m		2.24s	5.5b
(17b)		NHAc	92	154—156		48.6	3.9	19.1	$C_{12}H_{11}ClN_4O_3$	48.9	3.8	19.0	6.22s (4 H)	7.42—8.17m (+NH)		3.28s (Me)	1.95s
(17c)		Ph	82	150—152	150 [44]								6.90s (4 H)	7.67—8.17m		7.17—7.67m	

(NH_2). This amine (2.0 g) and acetic anhydride (5 ml) were heated together under reflux for 5 min and then water (20 ml) added and the solution re-boiled for 5 min. On cooling the yellow solid was filtered off, washed with water, dried and recrystallised from ethanol to give the *title product* (2.1 g, 92%), as cream crystals.

(g) 1-(5-Chloro-2-nitrophenyl)-3,5-diphenylpyrazole (17c) was prepared by the literature method.[44]

Reduction of the Nitrophenylpyrazoles.—The nitrophenylpyrazoles in Table 8 were reduced in ethanolic solution by hydrogenation under pressure using Raney nickel in an autoclave to give the amines recorded in Table 9.

Preparation of the Azidophenylpyrazoles.—The amine (0.05M) in a mixture of concentrated hydrochloric acid (15 ml) and water (15 ml) was cooled to 0° and diazotised with sodium nitrite (4.1 g, 0.06M) in water (10 ml). The resulting solution was added to a stirred ice-cold solution of sodium azide (3.9 g, 0.06M) in saturated aqueous sodium acetate (100 ml). After a further 1 h the mixture was extracted thoroughly with ether and the extract washed with aqueous sodium hydroxide (2M) and water, and then dried ($MgSO_4$). This solution was filtered through a short (10 cm) column of alumina and evaporated at 20° *in vacuo* to give the required azide, recorded in Table 9.

Deoxygenation of the Nitrophenylpyrazoles.—The nitro-compound (0.02M) in the appropriate solvent (190 ml, freshly distilled and eluted through alumina before use) was purged with nitrogen under reflux. To this solution was added triethyl phosphite (8.4 g, 0.05M) in the same solvent (10 ml). The mixture was stirred under reflux and nitrogen until the nitro-compound was consumed (monitored by h.p.l.c.; normally *ca.* 72 h). Removal of the volatile material on a rotary evaporator left a brown oil, which was chromatographed on alumina. Elution with light petroleum gave successively the pyrazolobenzotriazole followed by the pyrazoloquinoxaline and the amine. Elution with toluene or ether gave further intractable oils. The products are recorded in Tables 1 and 2, and in Schemes 1 and 3, and their properties are noted in Table 10.

Manganese Dioxide Oxidation of 1-(2-*Amino*-5-*chlorophenyl*)-3,5-*dimethylpyrazole* (3; Y = 5′-Cl).—The title pyrazole (2.70 g) was stirred in carbon tetrachloride (200 ml) with activated manganese dioxide (30 g made by decomposition of manganous oxalate at *ca.* 250°) under reflux for 54 h. The hot solution was filtered and the residue washed with chloroform and the combined filtrate evaporated. The resulting dark brown oil was chromatographed on alumina, when elution with petroleum gave 8-chloro-2-

TABLE 9

Properties of the aminophenylpyrazoles (3), (14) and (18) and the azidophenylpyrazoles (4) and (13)

Compound No.	Y	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	Chemical shift δ(CDCl₃) (J/Hz) Pyrazole ring	Benzene ring	Y	NH_2
(3)	H	93	92—94 [a]								2.14s and 2.19s (Me), 5.91s (4 H)	6.55—7.2m		3.91br
(3)	5′-Cl	97	108—110	59.5	5.4	18.8	$C_{11}H_{12}ClN_3$	59.6	5.5	18.95	2.12s and 2.27s (Me), 6.03s (4 H)	6.6—6.8m and 7.1—7.36m		4.11br
(3)	5′-Br	100	189—191	49.5	4.7	15.9	$C_{11}H_{12}BrN_3$	49.6	4.5	15.8	2.44br s (Me), 6.5s (4-H)	6.8—8.0m		5.65br
(3)	5′-NMe_2	98	111—112	67.7	7.8	24.45	$C_{13}H_{18}N_4$	67.8	7.9	24.3	2.14 and 2.27s (Me), 5.98s (4-H)	6.51—6.9m	2.78s	3.5br
(3)	4′-CF_3	100	85—86	56.7	4.6	16.6	$C_{12}H_{12}F_3N_3$	56.5	4.7	16.5	2.10s and 2.25s (Me), 5.93s (4-H)	6.7—7.25m		4.3br
(14)		97	Oil								0.74—1.47m (Me), 2.1—2.9m (CH_2), 5.97s (4 H)	6.19—7.27m		
(18) *		74	49	68.0	6.0	25.95	$C_9H_9N_3$	67.9	5.7	26.4	6.30 (4 H, *J* 2.0)	6.47—7.8m		4.9br
(18a)		96												
(4)	5′-Cl	91	72—74	53.4	4.1	28.5	$C_{11}H_6ClN_5$	53.3	4.1	28.3	2.18s and 2.34s (Me), 6.09s (4 H)	7.14—7.67m		
(4)	5′-Br	93	74—76	45.4	3.5	23.9	$C_{11}H_{10}BrN_5$	45.2	3.45	24.0	2.12s and 2.27s (Me), 5.85s (4 H)	6.8—7.54m		
(4)	5′-NMe_2	78	78—79	60.8	6.2	33.0	$C_{13}H_{16}N_6$	60.9	6.3	32.8	2.15s and 2.32s (Me), 6.13s (4 H)	6.7—7.24m	2.11s	
(4)	4′-CF_3	89	75—77	51.0	3.7	24.7	$C_{12}H_{10}F_3N_5$	51.2	3.6	24.9	2.14s and 2.27s (Me), 5.97s (4 H)	2.55s		
(13)		91	Oil								0.90—1.47q (Me), 2.16—2.9m (CH_2), 5.94s (4 H)	6.87—7.47m		
(18) *		79	Oil								6.49t (4 H, *J* 2.5)	7.2—8.17m		
(18c)											7.34—7.7m (Ph), 7.79s (4 H)	7.8—8.17m		

[a] Lit.,[43] 91°.

* H in place of Cl; $R^1 = R^2 = H$, see ref. 7 for further details.

methylpyrazoloquinoxaline (9; Y = 8-Cl) (0.4 g, 19%) followed by some starting material (0.6 g).

Control Experiments.—(a) 1-(5-Chloro-2-nitrophenyl)-3,5-dimethylpyrazole (3; Y = 5′-Cl) (5.0 g) in cumene (200 ml) was heated under reflux for 5 days under nitrogen giving solely starting material on evaporation (h.p.l.c.).

(b) 8-Chloro-1,3-dimethylpyrazolo[1,2-*a*]benzotriazole (8; Y = 8-Cl) (0.5 g) was refluxed in cumene (50 ml) under nitrogen for 24 h, yielding on evaporation the starting material only (h.p.l.c.).

(c) Experiment (b) was repeated in the presence of TEP (5.0 g) giving the same result.

(d) When experiment (b) was repeated using diglyme in place of cumene, the same result was noted.

(e) When experiment (b) was repeated with oxygen bubbling through the solution, after only 2 h reflux examination by t.l.c. indicated the formation of several products.

Synthesis and Thermolysis of Triethyl N-4-*Chloro*-2-(3,5-*dimethylpyrazol*-1-*yl*)-*phenylphosphorimidate.*—A solution of freshly distilled triethyl phosphite (20 ml) in dry benzene (10 ml) was added under nitrogen, to a refluxing solution of 1-(2-azido-5-chlorophenyl)-3,5-dimethylpyrazole (4; Y = 5′-Cl) (3.9 g) in dry benzene (100 ml) and the solution was allowed to reflux overnight. Removal of the solvent *in*

TABLE 10

Properties of the pyrazolobenzotriazoles (6), (8), (15), and (19) and the pyrazoloquinoxalines (9) and (16)

Compound No.	Y	M.p. (°C)	Cryst. solvent *	Found (%) C	H	N	Formula	Required (%) C	H	N	Chemical shift δ(CDCl$_3$) (*J*/Hz) Pyrazole ring	Benzenoid ring	Others
(6a)		102 †	A								6.66t (2 H, *J* 3.0)	6.92—7.6m	
(6b)											6.77t (2 H, *J* 3.0)	7.3—7.6m	
(6c)		158—159.5	A	70.0	5.5	24.5	$C_{10}H_9N_3$	70.15	5.3	24.5	6.51d (2 H, *J* 3.0), 25.7s (Me)	6.64—7.7m	
(6d)		180—181	A	58.3	3.9	20.6	$C_{10}H_8ClN_3$	58.4	3.9	20.4	6.62d (2 H, *J* 3.0), 2.61s (Me)	7.19—7.7m	
(8)	8-Cl	156—158	A	60.4	4.5	19.1	$C_{11}H_{10}ClN_3$	60.15	4.6	19.1	2.50s and 2.61s (Me), 6.25s (2 H)	7.2—7.34m and 7.47—7.57m	
(8)	8-Br	151—152	A	49.85	3.9	16.3	$C_{11}H_{10}BrN_3$	50.0	3.8	15.9	2.54s and 2.62s (Me), 6.28s (2 H)	7.34—7.69m	
(8)	8-Cl	91—92	A	59.95	4.5	19.2	$C_{11}H_{10}ClN_3$	60.15	4.6	19.1	2.47s and 2.52s (Me), 6.18s (2 H)	6.60d (8 H), 7.12dd (7 H), 7.37br, s (5 H)	
(8)	7-CF_3	138—139	A	56.8	3.9	16.7	$C_{12}H_{10}F_3N_3$	56.9	4.0	16.6	2.45s and 2.54s (Me), 6.21s (2 H)	6.80—7.05m, 7.3—7.67m	
(8)	7-NO_2	227—228	A	57.4	4.0	24.0	$C_{11}H_{10}N_4O_2$	57.4	4.4	24.3	2.60s and 2.81s (Me), 6.55s (2 H)	7.3—7.84m, 8.12—8.24m	
(8)	7-Me	65—67	A	72.4	6.65	21.0	$C_{12}H_{13}N_3$	72.3	6.6	21.1	2.45s and 2.51s (Me), 6.15s (2 H)	6.51—6.79mm, 7.2—7.53m	2.51s (Me)
(15)		76—78	A	6.28	5.6	17.2	$C_{13}H_{14}ClN_3$	63.0	5.7	17.1	2.30t (Me) 2.50—3.18m (CH_2), and 6.20s (2 H)	7.07—7.47m	
(19c)		212—214	B	73.2	4.0	12.5	$C_{21}H_{14}ClN_3$	73.4	4.1	12.2	7.37—7.94m (Ph), 7.30s (2 H)	8.24—8.59m	
(9)	8-Cl	150—152	A	60.6	3.8	19.2	$C_{11}H_8ClN_3$	60.7	3.7	19.3	2.64s (Me), 6.75s (3 H)	7.52dd (7 H), 8.11d (6 H), 8.60d (9 H) (*J* 8 and 2.5)	9.00s (4 H)
(9)	8-Br	181—183	A	50.1	3.1	15.8	$C_{11}H_8BrN_3$	50.4	3.1	16.0	2.50s (Me), 6.52s (3 H)	7.10—7.94m, 8.40d (*J* 2) (9 H)	8.85s (4 H)
(9)	8-NMe_2	118—119	A	68.8	6.1	25.0	$C_{13}H_{14}N_4$	69.0	6.2	24.8	2.42 (Me), 6.36s (3 H)	6.75dd (7 H), 7.32d (9 H), 7.76d (6 H) (*J* 9 and 2.5)	8.56 (4 H), 2.89s (NMe_2)
(9)	8-OMe	77—79	A	67.2	5.0	19.6	$C_{12}H_{11}N_3O_2$	67.6	5.2	19.7	2.47s (Me), 6.34s (3 H)	6.90dd (7 H), 7.47d (9 H), 7.71d (6 H) (*J* 9 and 2.5)	8.54s (4 H), 3.85s (OMe)
(9)	7-CF_3	161—163	A	57.6	3.3	17.0	$C_{12}H_8F_3N_3$	57.4	3.2	16.7	2.57s (Me), 6.67s (3 H)	7.82d (9 H), 8.15—8.60m (6 H and 8 H)	8.90s (4 H)
(16)		96—97	A	63.4	4.6	7.0	$C_{13}H_{12}ClN_3$	63.55	4.9	17.1	2.79q and 1.33t (Et, *J* 7), 6.39s (3 H)	7.05—8.2m	2.56s (Me)

* A = petroleum, B = ethyl acetate. † Lit.,[3] 102°.

vacuo gave a pale yellow liquid which on distillation gave the *title phosphorimidate*, b.p. 174—176° at 0.15 mmHg, as an oil (3.6 g, 59%) (Found: C, 53.0; H, 6.5; N, 10.7. $C_{17}H_{25}ClN_3O_3P$ requires C, 52.9; H, 6.5; N, 10.9%), *m/e* 385—387 (M^+), δ($CDCl_3$) 6.84—7.4(m, aromatic), 5.93 (4 H, s, pyrazole), 3.98 (q, CH_2, *J* 7 Hz), 2.25 and 2.16 (2 × s, pyrazole Me), and 1.23 (t, Me, *J* 7 Hz). The phosphorimidate (3.6 g) in cumene (200 ml) under nitrogen was unchanged after 24 h reflux (h.p.l.c.).

Photolysis of the Azides.—Using the apparatus described at the beginning of the Experimental section, with water cooling for ambient temperature reactions and n-butanol under reflux (by the heat of the lamp) for reactions at 107°, pure nitrogen was flushed through the solution for 15 min prior to irradiation. The reaction was monitored by following the disappearance of the azide i.r. absorption (2 100—2 160 cm^{-1}) in samples removed through a rubber septum, the reaction time at ambient temperature being normally *ca.* 72 h, and at 107°, *ca.* 8—12 h. The reaction mixture was worked up as described for the deoxygenation experiments. Pyrene (3.0 g) was removed by initial elution with light petroleum on alumina. The usual products were obtained using petroleum as described above. Photolysis of 1-(2-azidophenyl)pyrazole in acetophenone gave 2,2′-bis(pyrazol-1-yl)azobenzene (35%), m.p. 166—167° (lit.,[3] 167°), as well as 1-(2-aminophenyl)pyrazole (16%). 8-Chloro-1,3-dimethylpyrazolo[1,2-*a*]benzotriazole (8; Y = 8-Cl) (0.6 g) on photolysis is acetophenone at ambient temperature was unchanged after 72 h (h.p.l.c.).

Kinetics of the Thermolysis of 1-(2-*Azido*-5-*chlorophenyl*)-3,5-*dimethylpyrazole* (4; Y = 5′-Cl).—A solution of the title azide (2.475 g) in the solvent (5.0 ml) was rapidly added to the stirred heated solvent (45.0 ml) under nitrogen in an apparatus surrounded with a glass outer jacket in which cumene was refluxed. Samples were removed through a rubber septum with a long-needled syringe at 10-min intervals and the rapidly cooled solutions were examined by i.r. spectroscopy, measuring the absorption at 2 120 cm^{-1}. The peaks were cut out and weighed and compared with calibration graphs of weights against known concentrations. In all ten samples were taken, and each experiment repeated. The runs were conducted in the same apparatus with both cumene and diglyme as solvent. The solvents were purified as described in the Discussion section, and gave the results already discussed.

Preparation of the N-(2-*Nitrophenyl*)*tetrahydroindazoles* (20) *and* (24).—The following methods were employed to prepare the title compounds giving products as outlined in Table 7.

1. The method described by Tsuge and Samura [19,20] was used. The crude product was chromatographed on alumina when elution with petroleum–toluene (1 : 1) gave a yellow solid, m.p. 96° (lit.,[19] 94—96°).

2. A mixture of 4,5,6,7-tetrahydroindazole [47] (24.4 g), 2-fluoronitrobenzene (28.2 g), and anhydrous potassium fluoride (14.1 g) was stirred and heated at 120—130° for 24 h. The resulting brown oil was dissolved in chloroform (500 ml), filtered, and chromatographed on alumina. Elution with ethyl acetate gave a yellow solid (15.5 g), m.p. 126—128°.

3. A mixture of 4,5,6,7-tetrahydroindazole (3.4 g), 2-bromonitrobenzene (9.8 g), anhydrous potassium carbonate (0.42 g), copper(I) bromide (0.2 g), and nitrobenzene (80 ml) was heated and stirred under reflux for 28 h.[21] The resulting mixture was steam-distilled to remove nitrobenzene and the excess of bromonitrobenzene and the residue extracted with chloroform. Chromatography of the tarry residue as in method 2 gave no identifiable products.

4. A mixture of 4,5,6,7-tetrahydroindazole (6.0 g) and silver nitrate (8.5 g) in concentrated aqueous ammonium hydroxide (*d* 0.880; 20 ml) was stirred at 0° for 2 h.[22] The resulting black amorphous solid was filtered and washed with ammonium hydroxide and the dried residue heated with a mixture of 2-fluoronitrobenzene (7.1 g) and anhydrous potassium fluoride (3.5 g) at 120—140° for 24 h. The cooled reaction mixture was extracted with chloroform–ethanol (1 : 1 v/v) and the filtrate evaporated. The residue was triturated with light petroleum to give a brown solid (11.9 g) which crystallised from petroleum (b.p 80—100°) to give fawn crystals, m.p. 96—98°.

5. Thallium(I) ethoxide (13.0 g) was added dropwise to a solution of 4,5,6,7-tetrahydroindazole (6.6 g) in warm petroleum (50 ml). The resulting pale brown emulsion was heated with 2-fluoronitrobenzene (7.1 g) at 120—140° for 24 h, the petroleum being removed in the first few minutes of heating. The cooled reaction mixture was extracted with chloroform and the extract absorbed onto alumina and eluted with toluene to give a pale brown oil (12.1 g) which crystallised on standing. Recrystallisation from petrol (b.p. 80—100°) gave the product as fawn crystals, m.p. 95—97°.

6. A solution of 2-nitrophenylhydrazine hydrochloride (9.45 g) in aqueous ethanol (50%, 100 ml) was added with stirring to a solution of 2-hydroxymethylenecyclohexanone [47] (6.3 g) in ethanol (20 ml) at 0°. A red solid precipitated immediately. Concentrated sulphuric acid (98%; 10 ml) was added and the mixture refluxed for 4 h. On cooling and addition of water (200 ml) a yellow solid precipitated which was filtered off, washed with water, and dried (11.4 g). Recrystallisation from petrol (b.p. 80—100°) gave the product as pale yellow crystals, m.p. 127—129°. The above products were examined by h.p.l.c. A 10-μg sample in chloroform solution was examined on an HP silica column (30 cm long × 3.9 mm) (10 μm particle size; plate count >2 500) eluting with chloroform–iso-octane (15 : 85) at 4 ml min^{-1}. Two peaks at 59 and 109 mm from the injection point were observed and assigned to 2-(2-nitrophenyl)-4,5,6,7-tetrahydroindazole and the corresponding 1-isomer, respectively, on the basis of products from deoxygenation with TEP. The analysis was repeated preparatively. Pure 1-(2-*nitrophenyl*)-4,5,6,7-*tetrahydroindazole* (20) was obtained as pale yellow crystals from petrol (b.p. 80—100°), m.p. 130° (Found: C, 64.3; H, 5.5; N, 17.1. $C_{13}H_{13}N_3O_2$ requires C, 64.2; H, 5.4; N, 17.3%), δ($CDCl_3$) 1.65—2.1 (m, 2 × CH_2), 2.4—2.8 (m, 2 × CH_2), and 7.4—8.17 (m, aromatic). 2-(2-Nitrophenyl)-4,5,6,7-tetrahydroindazole (24) was erroneously described by Tsuge and Samura [19] as the 1-isomer.

Deoxygenation of the 2-*Nitrophenyl*-4,5,6,7-*tetrahydroindazoles.*—The above nitro-compounds (4.8 g) were deoxygenated as described earlier with TEP (8.4 g) in cumene (200 ml) for 5 days. Volatile matter was then removed *in vacuo* and the residual brown oily solid chromatographed on alumina From the mixture of nitro-compounds produced in method 2 the following products were obtained. Elution with petrol (b.p. 80—100°) gave N-*ethylindazoloquinoxaline* (27) (2.2 g, 47%), m.p. 129—130° [from petrol (b.p. 80—100°)] (Found: C, 75.2; H, 7.1; N, 17.85. $C_{15}H_{17}N_3$ requires C, 75.3; H, 7.2; N, 17.5%), δ($CDCl_3$) 1.09 (t, Me, *J* 7 Hz), 1.25—2.63 (m,

3 × CH_2), 3.34 (q, CH_2, *J* 7 Hz), 4.17br (t, CH, *J* 5 Hz), 6.65—7.3 (m, 3 aromatic H), 7.50 (s, pyrazole H), and 7.89 (dd, 1 aromatic H, *J* 7 and 2 Hz). Further elution with the same solvent gave the indazolobenzotriazole (28) (0.04 g, 1%), m.p. 148—150° [from petrol (b.p. 80—100°)] (lit.,[19] 149—150°, assigned to the isomeric indazolobenzotriazole in error). Further elution with toluene gave 1-(2-nitrophenyl)-4,5,6,7-tetrahydroindazole (0.33 g, 8%), identical with that described below.

From 2-(2-nitrophenyl)-4,5,6,7-tetrahydroindazole (1.5 g) with TEP (2.7 g) in cumene (65 ml) an orange oil was obtained, which on chromatography on alumina gave with toluene the indazolobenzotriazole (0.25 g, 19%), m.p. 148—150°, identical to that described above. Further elution with toluene gave 2-(2-aminophenyl)-4,5,6,7-tetrahydroindazole (0.13 g, 10%), identical to that described below.

Reduction of the Nitrophenylindazoles.—The nitro-compounds were reduced, by the method described for the nitrophenylpyrazoles, to give (a) 1-(2-aminophenyl)-4,5,6,7-tetrahydroindazole (22) (84%) as an oil, $\nu_{max.}$ 3 440 and 3 500 cm^{-1} (NH_2), δ($CDCl_3$) 1.57—2.0 (m, 2 × CH_2), 2.3—3.0 (m, 2 × CH_2), 3.44br (NH_2), and 6.6—7.87 (m, aromatic H , and (b) 2-(2-aminophenyl)-4,5,6,7-tetrahydroindazole (26) as an oil, $\nu_{max.}$ 3 490 and 3 440 cm^{-1} (NH_2), δ($CDCl_3$) 1.5—2.1 (m, 2 × CH_2), 2.44—3.1 (m, 2 × CH_2), 4.42br (NH_2), and 6.5—7.57 (m, aromatic H). (c) The above mixtures of nitro-compounds were similarly reduced. In all cases the amines were used without further purification.

Preparation of the Azides (21) *and* (25).—The above amines were converted into azides in the manner described above for the azidophenylpyrazoles. The azide obtained from the mixture of nitro-compounds prepared by method 2 gave a brown solid which was purified by chromatography on alumina. Elution with diethyl ether gave the *azide* as yellow crystals (6.1 g, 92%), m.p. 72—74° (from petroleum) (Found: C, 65.0; H, 5.1; N, 29.2. $C_{13}H_{13}N_5$ requires C, 65.25; H, 5.5; N, 29.3%), $\nu_{max.}$ (Nujol) 2 130 cm^{-1} (N_3), δ($CDCl_3$) 1.44—2.06 (m, 2 × CH_2), 2.22—3.02 (m, 2 × CH_2), and 7.1—7.84 (m, aromatic H).

Decomposition of the 2-Azidophenyltetrahydroindazoles.—Thermolyses and photolyses were conducted as described above for the pyrazoles on the above azide giving the following products by chromatography on alumina.

(a) *Thermolysis in cumene.* Elution with toluene gave 1-(2-aminophenyl)-4,5,6,7-tetrahydroindazole (14%) and no other recognisable products.

(b) *Photolysis in dichloromethane.* Elution with petroleum gave *2,2'-bis-(4,5,6,7-tetrahydroindazol-1-yl)azobenzene* (28%) as orange crystals from petrol (b.p. 80—100°), m.p. 235—236° (Found: C, 73.9; N, 6.1; N, 20.0. $C_{26}H_{26}N_6$ requires C, 73.9; H, 6.2; N, 19.9%), *m/e* 422 (M^+), δ($CDCl_3$) 1.5—2.02 (m, 2 × CH_2), 2.39—3.0 (m, 2 × CH_2), and 7.0—8.04 (m, aromatic H). Further elution with toluene gave the indazolobenzotriazole (28) (5%), identical with that described above, followed by 1-(2-aminophenyl)-4,5,6,7-tetrahydroindazole (22) (11%).

(c) *Photolysis in acetophenone.* Elution with petroleum gave the azo-compound described in (b) (45%) followed by the amine (22) (22%) described in (b) on elution with toluene.

Preparation of Precursors to 1-(2-*Carbenophenyl*)-3,5-*dimethylpyrazole* (29).—(a) 2-(3,5-*Dimethylpyrazol*-1-*yl*)-*benzaldehyde* (38). To a solution of 1-phenyl-3,5-dimethylpyrazole [48] (37) (8.6 g, 0.05M) in dry diethyl ether (50 ml) was added, under nitrogen with stirring at 0°, n-butyllithium in hexane (0.05M). The resulting solution was stirred for a further 1 h when dimethylformamide (3.65 g, 0.05M) in diethyl ether (10 ml) was added. After a further 30 min at ambient temperature, water (25 ml) was added. The resulting precipitate was filtered off and the ether phase dried and evaporated to yield a further crop of product. The combined material was crystallised from diethyl ether as crystals of 2-(3,5-*dimethylpyrazol*-1-*yl*)*benzaldehyde* (38) (7.5 g, 75%), m.p. 118—120°, $\nu_{max.}$ (Nujol) 1 695 cm^{-1} (CHO), δ($CDCl_3$) 2.15 (s) and 2.30 (s) (Me), 6.05 (s, pyrazole CH), 7.25—8.15 m, (aromatic H), and 9.65 (s, CHO), *m/e* 200 (M^+, 9%), 172 (M^+ — CO, 100), 171 (M^+ — CHO, 68), 130 (26), and 77 (18) (Found: C, 71.9; H, 6.0; N, 14.1. $C_{12}H_{12}N_2O$ requires C, 72.0; H, 6.0; N, 14.0%).

(b) 2-(3,5-*Dimethylpyrazol*-1-*yl*)*benzaldehyde* p-*tolylsulphonylhydrazone* (31). To the above aldehyde (38) (2.0 g, 0.01M) in ethanol (25 ml) was added *p*-tolylsulphonylhydrazine (1.9 g, 0.01M) and acetic acid (4 drops) in ethanol (5 ml) and the mixture heated for 30 min. The solution was cooled, poured into ice, and the precipitate filtered off and recrystallised from ethanol to give the *title hydrazone* (31) (3.4 g, 93%) as crystals, m.p. 164—165° (decomp) (Found: C, 61.7; H, 5.7; N, 15.2. $C_{19}H_{20}N_4O_2S$ requires C, 61.9; H, 5.5; N, 15.2%), δ($CDCl_3$) 1.95 (s) and 2.05 (s) (pyrazole Me) 2.35 (s, phenyl Me), 3.95 (s, pyrazole CH), and 7.05—8.15 (m, aromatic H and CH=N).

(c) *Diazo*-2-(3,5-*dimethylpyrazol*-1-*yl*)*phenylmethane* (32). (i) The above sulphonylhydrazone (31) (1.89 g, 0.005M), sodium methoxide (0.54 g, 0.01M), and pyridine (20 ml) were stirred together at 40° for 2 h, when the solvent was removed *in vacuo*. The residue showed i.r. absorptions at 2 090 and 1 045 cm^{-1} indicative of $-CHN_2$ but was mostly unchanged hydrazone (t.l.c.). Reaction at 60° gave much tar.

(ii) To a solution of 2-(3,5-dimethylpyrazol-1-yl)benzaldehyde (38) (2.0 g, 0.01M) in ethanol (25 ml) was added hydrazine hydrate (0.5 g, 0.01M) and the solution heated under reflux for 30 min. The cooled solution was poured into water (50 ml) and extracted with diethyl ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$) and evaporated at ambient temperature to give the *hydrazone* (39) as an oil (1.8 g, 84%), $\nu_{max.}$ 3 380, 3 330, and 3 200 cm^{-1} (NH_2), δ 5.75 (s, pyrazole CH) and 6.5—7.95 (m, aromatic H). Heat, chromatography, or time resulted in the quantitative conversion of the hydrazone into the azine (34).

(iii) The hydrazone (39) (2.14 g, 0.01M) in diethyl ether (20 ml) was treated successively at 0° with magnesium sulphate (4 g), ethanolic potassium hydroxide (5 drops, 40%), and yellow mercury(II) oxide (4.0 g) (added over 10 min). The mixture was stirred for 24 h at ambient temperature, filtered, and evaporated at 0—10° to yield a mixture of the starting material and the required diazomethane as indicated by i.r.

(iv) To a solution of the hydrazone (39) (2.14 g, 0.01M) in diethyl ether (20 ml) at 0° was added magnesium sulphate (4 g), ethanolic potassium hydroxide (5 drops, 40%), and silver(I) oxide (2.0 g). After 30 min at ambient temperature the mixture was filtered to give a product free of starting material (solution i.r.), this solution being used directly.

Decomposition of the Carbene Precursors (31) *and* (32).—(a) *Decomposition of the tolylsulphonylhydrazone* (11). The *p*-tolylsulphonylhydrazone (31) (5.5 g, 0.015M) in diglyme (10 ml) was added dropwise to a stirred suspension of sodium methoxide (1.6 g, 0.03M) in boiling diglyme (40 ml). The mixture was heated at reflux for a further 15 min and

evaporated *in vacuo*. The brown residue was chromatographed on alumina when elution with light petroleum–chloroform yielded 2,2′-*bis*-(3,5-*dimethylpyrazol*-1-*yl*)*benzaldehyde azine* (1.35 g, 46%) as yellow crystals from ethanol, m.p. 237—239° (Found: C, 72.9; H, 6.1; N, 21.9. $C_{24}H_{24}N_6$ requires C, 72.7; H, 6.1; N 21.2%), $\nu_{max.}$ (Nujol) 1 625 cm^{-1} (C=N), δ($CDCl_3$) 2.05 (s) and 2.28 (s) (Me), 5.95 (s, pyrazole CH), 7.1—7.65 (m, aromatic H), and 7.95—8.35 (m, 1 aromatic H and CH=N), *m/e* 396 (M^+, 0.5%), 198 (58), 185 (33), 184 (100), 183 (26), and 143 (20). Further elution with the same solvent gave 2-(2,5-*dimethylpyrazol*-1-*yl*)*benzyl alcohol* (35) (0.3 g, 10%) as crystals from toluene, m.p. 112—113° (Found: C, 71.1; H, 7.0; N, 14.05. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 7.0; N, 13.85%), $\nu_{max.}$ (Nujol) 3 230 cm^{-1} (OH), δ($CDCl_3$) 2.10 (s) and 2.20 (s) (Me), 4.15 (s, CH_2), 5.0br (OH), 5.95 (s, pyrazole CH), 6.85—7.65 (m, aromatic H), 202 (M^+, 99%), 173 (58), 171 (36), 160 (100), 159 (54), 146 (36), 132 (34), 130 (32), 117 (31), 83 (39), and 77 (51).

(b) *Decomposition of the diazomethane* (32). A solution containing the diazomethane (0.01M) in diethyl ether (150 ml) was irradiated at ambient temperature as for the azides above, but using a quartz filter since no reaction occurred with Pyrex equipment. After 24 h the solution was free of starting material (i.r.) and was evaporated and chromatographed on alumina. Elution with light petroleum–chloroform yielded 2,2′-bis-(3,5-dimethylpyrazol-1-yl)benzaldehyde azine (34) (0.65 g, 33%) identical to that reported above.

Unambiguous Syntheses.—(a) *The azine* (34). To a solution of the benzaldehyde (38) (2.0 g, 0.01M) in ethanol (25 ml) was added hydrazine hydrate (0.25 g, 0.005M) and the mixture refluxed for 30 min. On cooling a crystalline solid precipitated and was filtered off and recrystallised from ethanol to give the title product (1.6 g, 81%), m.p. 237—239°, identical with that already reported.

(b) *The benzyl alcohol* (35). The aldehyde (38) (2.0 g, 0.01M) was added to a stirred suspension of lithium aluminium hydride (0.19 g, 0.05M) in dry ether (30 ml) under nitrogen. After 2 h reflux moist ether was carefully added, followed by aqueous sodium hydroxide (4M, 5 ml). The mixture was extracted with ether (3 × 30 ml) and the combined extracts dried ($MgSO_4$) and evaporated. The residual solid was recrystallised from toluene to give the title product (2.0 g, 99%), m.p. 112—113°, identical with that reported previously.

Preparation of the Sulphonyl Azide (33).—(a) *Attempted condensation reactions with* 3,5-*dimethylpyrazole*. To 3,4-dimethylpyrazole (9.6 g, 0.1M) in ethanol (50 ml) was added sodium 2-chloro-5-nitrobenzenesulphonate (26.0 g, 0.1M) in water (20 ml) and the mixture heated under reflux for 24 h. Removal of the solvent gave only unchanged starting materials. The reaction was repeated in DMSO and neat under reflux, again with no effect. Finally the neat reagents were heated with potassium acetate and copper(II) acetate (1 molar proportion of each) under nitrogen at 200° for 24 h. Only unchanged material was again isolated.

(b) *By metallation of* 1-*phenyl*-3,5-*dimethylpyrazole* (37). A solution of 2-(3,5-dimethylpyrazol-1-yl)phenyl-lithium (0.05M) was made as described above. Dry sulphur dioxide was rapidly bubbled into this solution at 0° resulting in a precipitate (*ca.* 15 min). After 1 h stirring, nitrogen was bubbled through the mixture for 10 min, followed by addition of *N*-chloroacetamide (4.7 g, 0.05M) and the mixture stirred for 15 h at ambient temperature. The mixture was filtered and the filtrate evaporated to give an oil which was added to hydrazine hydrate (2.5 g, 0.05M) in diethyl ether (20 ml). After 30 min stirring the solvent was again removed and the oily solid residue purified by recrystallisation from petroleum to give 2-(3,5-*dimethylpyrazol*-1-*yl*)*phenylsulphonylhydrazide* (43) (4.0 g, 30%) as plates, m.p. 132° (decomp) (Found: C, 50.05; H, 5.4; N, 21.1. $C_{11}H_{14}N_4O_2S$ requires C, 49.6; H, 5.3; N, 21.0%), $\nu_{max.}$ (Nujol) 2 415, 3 295, and 3 195 cm^{-1} (NH, NH_2), δ($CDCl_3$) 2.12 (s) and 2.26 (s) (Me), 4.35br (NH_2), 6.05 (s, pyrazole CH), 7.20br (NH), 7.1—7.9 (m, aromatic H), and 9.12—9.30 (m, 1 aromatic H), *m/e* 266 (M^+, 2%), 172 (100), 171 (67), and 77 (33). This hydrazide (2.7 g, 0.01M) in aqueous hydrochloric acid (20 ml, 4M) at 0° was diazotised with sodium nitrite (1.4 g, 0.02M) in water (10 ml) below 5°. After 30 min the solution was neutralised by addition of aqueous sodium hydroxide (4M) and extracted with ether (3 × 50 ml). The extracts were dried ($MgSO_4$) and evaporated and the residual yellow solid recrystallised from light petroleum to give 2-(3,5-*dimethylpyrazol*-1-*yl*)*benzenesulphonyl azide* (33) (2.05 g, 74%) as needles, m.p. 90—91° (decomp. point 144°) (Found: C, 47.9; H, 4.1; N, 25.0. $C_{11}H_{11}N_5O_2S$ requires C, 47.65; H, 4.0; N, 25.3%), $\nu_{max.}$ (Nujol) 2 160 cm^{-1} (N_3), δ($CDCl_3$) 2.09 (s) and 2.25 (s) (Me), 6.04 (s, pyrazole CH), 7.35 (dd, 1 aromatic H, *J* 7 and 2 Hz), 7.69 dq, 2 aromatic *J* 8, 7, and 2 Hz), 8.16 (dd, 1 aromatic H, *J* 8 and 2 Hz), *m/e* 277 (M^+, 100%), 235 (48) 184 (79), 172 (58), 171 (62), 157 (43), 156 (20), 143 (27), 130 (52), 129 (52), 117 (59), 103 (26), 90 (24), 77 (96), and 76 (41).

(c) *By the attempted interaction of the sulphonyl chloride* (42) *with sodium azide*. A solution of 2-(3,5-dimethylpyrazol-1-yl)benzenesulphonyl chloride (0.05M) obtained as in (b) was added to a solution of sodium azide (3.25 g, 0.05M) in ethanol (20 ml) and the mixture stirred for 1 h. Dilution with water (50 ml) and extraction with ether (4 × 50 ml) gave, on drying ($MgSO_4$) and evaporation, an oil which solidified on trituration with chloroform. The solid proved to be 2-(3,5-*dimethylpyrazol*-1-*yl*)*benzenesulphonic acid* (36) (0.2 g, 2%) obtained as crystals from ethanol, m.p. 352° (Found: C, 52.3; H, 4.8; N, 11.05. $C_{11}H_{12}N_2O_3S$ requires C, 52.4; H, 4.8; N, 11.1%); δ ([$^2H_6$]DMSO) 2.10 (s) and 2.35 (s) (Me), 6.51 s, pyrazole CH), 7.3—8.1 (m, aromatic H), *m/e* 252 (M^+, 34%), 172 (95), 171 (100), 130 (27), and 77 (22). The chloroform-soluble material was chromatographed on alumina when elution with petroleum–diethyl ether gave first 1-phenyl-3,5-dimethylpyrazole (37) (0.8 g, 10%) followed by 2,2′-*bis*-(3,5-*dimethylpyrazol*-1-*yl*)*biphenyl* (47) (0.2 g, 3%) as crystals from light petroleum, m.p. 128°, $\nu_{max.}$ (Nujol) 762 cm^{-1} (*ortho*-disubstituted C_6H_4), δ($CDCl_3$) 1.95 (s) and 2.10 (s) (Me), 5.75 (s, pyrazole CH), 6.7—7.35 (m, aromatic H), $\lambda_{max.}$ (MeOH) 216sh (log ε 4.393), 231 (4.444), and 250 nm (4.198), *m/e* 342 (M^+, 100%), 341 (46), 327 (33), 247 (58), 171 (25), 80 (83), and 77 (17) (Found: M^+, 342.184 7. $C_{22}H_{22}N_4$ requires *M*, 342.184 4).

(d) *Attempted preparation of* 2-(3,5-*dimethylpyrazol*-1-*yl*)-*benzenesulphonyl chloride* (42) *from the lithium sulphinate* (41) *and chlorine*. (i) A solution of the lithium sulphinate (0.025M) prepared as in (b) was stirred at 0° and chlorine gas was bubbled in for 45 min giving a yellow solution with a white suspension. After a further 15 h the mixture was filtered and the filtrate evaporated to give a yellow solid. Recrystallisation from petroleum afforded crystals of 2-(4-*chloro*-3-*methyl*-5-*trichloromethylpyrazol*-1-*yl*)*benzene*-

sulphonyl chloride (44) (4.1 g, 40%), m.p. 122—123° (Found: C, 32.4; H, 1.7; N, 7.0. $C_{11}H_7Cl_5N_2O_2S$ requires C, 32.3; H, 1.7; N, 6.9%); δ($CDCl_3$) 2.25 (s, Me), 7.25—7.9 (m, 3 × aromatic H), and 8.0—8.35 (m, aromatic H), δ_C($CDCl_3$) 148.34 (s), 140.82 (s), 139.16 (s), 137.69 (s), 135.64 (d), 131.63(d), 131.34 (d), 130.27 (d), 112.50 (s, pyrazole C-Cl), 86.14 (s, CCl_3), and 11.42 (q, Me), *m/e* 406/408/410/412/414/416 (M^+, ratio 65 : 100 : 70 : 23 : 5 : 0.2. Cl_5 requires 60 : 100 : 67 : 22 : 4 : 0.3; *m/e* 406 3%), (only $^{35}Cl_n$ peak quoted for subsequent fragment peaks) 375 (34), 373 (38), 239 (58), 237 (100), 203 (23), 111 (15), 77 (15), and 75 (20).

(ii) To the lithium sulphinate salt (41) (0.025M) was added, dropwise at 0° with stirring over 0.5 h, a solution of chlorine (0.025M) in carbon tetrachloride. After stirring overnight the solution was filtered and dried ($MgSO_4$) and evaporated to give a yellow oil (5.0 g). ^1H N.m.r. spectroscopy revealed a complex mixture. The ratio of pyrazole 5-Me : 3-Me : 4-H was 0.5 : 1 : 0.08.

Decomposition of the Sulphonyl Azide (33).—The azide was thermolysed in chlorobenzene and in dimethyl sulphoxide solution as described above for the azidophenylpyrazoles, and the brown residues on evaporation of the solvent chromatographed on silica giving the products indicated in Scheme 6 and below. Unchanged azide (33) was eluted with chloroform and was followed by 1-phenyl-3,5-dimethylpyrazole. Further elution with chloroform gave *2(3,5-dimethylpyrazol-1-yl)benzenesulphonamide* (49) as crystals from chloroform, m.p. 185—186° (Found: C, 52.2; H, 5.2; N, 16.9. $C_{11}H_{13}N_3O_2S$ requires C, 52.55; H, 5.2; N, 16.7%). $\nu_{max.}$ (Nujol) 3 320 cm^{-1} (NH_2), δ($CDCl_3$) 2.10 (s) and 2.25 (s) (Me), 5.85br (NH_2), 5.90 (s, pyrazole CH), 7.05—7.80 (m, aromatic H), *m/e* 251 (M^+, 100%), 250 (32), 171 (71), 169 (28), 130 (28), 129 (93), and 77 (27). Further elution with ethyl acetate gave *1,3-dimethylpyrazolo[2,1-c]-1,2,3,4-benzothiatriazine 6,6-dioxide* (48) as crystals from chloroform, m.p. 222—223° (decomp), δ($CDCl_3$) 2.54 (s) and 2.70 (s) (Me), 6.30 (s, pyrazole CH), and 7.24—8.25 m, aromatic H), *m/e* 249 (M^+, 59%), 235 (M^+ — N, 92), 171 (M^+ — SO_2N, 96), 162 (26), 157 (95), 156 (63), 129 (23), 118 (86), 117 (99), 116 (36), 115 (48), 90 (42), 77 (99), 76 (100), and 75 (36) (Found: M^+, 249.056 8. $C_{11}H_{11}N_3O_2S$ requires *M*, 249.057 2. Found: M^+ — N, 235.054 6. $C_{11}H_{11}N_2O_2S$ requires 235.055 1. Found: M^+ — SO_2N, 171.092 2. $C_{11}H_{11}N_2$ requires M^+ — SO_2N, 171.092 2). Finally, elution with ethanol gave *2-(3,5-dimethylpyrazol-1-yl)benzenesulphonyl dimethylsulphoximide* (50) as a pale brown solid which decomposed on standing to an oil, $\nu_{max.}$ 1 060 and 1 010 cm^{-1} (S=O), δ(CF_3CO_2D) 2.50 (s) and 2.90 (s) (Me), 6.45 (s, pyrazole CH), 7.32—8.40 (m, aromatic H), *m/e* 327 (M^+, 4%), 171 (18), 94 (39), 80 (51), 79 (53), 78 (100), and 77 (13).

Unambiguous Synthesis of the Sulphonamide (49).—A solution of the sulphonyl chloride (42) (0.05M) prepared as described above was added to ammonium hydroxide (*d* 0.880; 25 ml) with stirring. After 30 min the precipitate was filtered and washed with water. Recrystallisation from chloroform gave the title product (2.2 g, 18%) as crystals, m.p. 185—186°, identical to that reported above.

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1 Part 7, D. G. Hawkins, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1979, 3207.
2 I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters*, 1976, 925.
3 B. M. Lynch and Y. Y. Hung, *J. Heterocyclic Chem.*, 1965, **2**, 218.
4 I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Research*, 1977, (*S*) 17, (*M*) 434.
5 J. M. Lindley, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1978, 1198.
6 O. Meth-Cohn and H. Suschitzky, *Chem. and Ind.*, 1969, 443.
7 J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1977, 2194.
8 L. Horner, A. Christmann, and A. Gross, *Chem. Ber.*, 1963, **96**, 399.
9 I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters*, 1976, 929.
10 J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.
11 J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters*, 1976, 4513.
12 R. Gleiter and R. Hoffmann, *Tetrahedron*, 1968, **24**, 5899.
13 G. R. Felt, S. Linke, and W. Lwowski, *Tetrahedron Letters*, 1972, 2037.
14 H. Takeuchi, Y. Kasamatsu, M. Mitani, Tsuchida, and K. Koyama, *J.C.S. Perkin I*, 1978, 780, 783.
15 T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes and Arynes,' Nelson, London, 1969.
16 P. Germaraad, W. Weyler, and H. W. Moore, *J. Org. Chem.*, 1974, **39**, 781.
17 J. S. Swenton, I. J. Ikeler, and B. H. Williams, *J. Amer. Chem. Soc.*, 1970, **92**, 3103.
18 B. Iddon, O. Meth-Cohn, E. F. V. Scriven, H. Suschitzky, and P. T. Gallagher, *Angew, Chem. Internat. Edn.*, in the press and references cited therein.
19 O. Tsuge and H. Samura, *Org. Prep. Procedures Internat.*, 1972, **4**, 273.
20 O. Tsuge and H. Samura, *J. Heterocyclic Chem.*, 1971, **8**, 707.
21 J. Elguero, A. Fruchier, and R. Jacquier, *Bull. Soc. chim. France*, 1967, 2619.
22 K. von Auers and W. Schaich, *Ber.*, 1921, **54**, 1738.
23 D. G. Farnum, *J. Org. Chem.*, 1963, **28**, 870.
24 W. Schroeder and L. Katz, *J. Org. Chem.*, 1954, **19**, 718.
25 W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 1952, 4735; R. Garner, *Tetrahedron Letters*, 1968, 221.
26 H. Reimlinger, *Chem. Ber.*, 1964, **97**, 339.
27 W. Kirmse in 'Carbene Chemistry,' Academic Press, New York, 1974, ch. 5.
28 D. S. Taylor, Ph.D. Thesis, University of Salford, 1971.
29 J. W. Wilt, C. A. Schneider, H. F. Dabek, J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, 1966, **31**, 1543.
30 J. Martin, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1974, 2451.
31 R. B. Scott, J. B. Gayle, M. S. Heller, and R. E. Lutz, *J. Org. Chem.*, 1955, **20**, 1165.
32 R. Fusco in 'The Chemistry of Heterocyclic Compounds, Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles and Condensed Rings,' ed. A. Weissberger, Interscience, New York, 1967, ch. 5.
33 R. Huttel, O. Schafer, and G. Welzel, *Annalen*, 1956, **598**, 186.
34 *E.g.* R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *J Amer. Chem. Soc.*, 1969, **91**, 1219.
35 D. S. Breslow, M. F. Sloan, N. R. Newburg, and W. B. Renfrow, *J. Amer. Chem. Soc.*, 1969, **91**, 2273.
36 H. Suschitzky, *J. Chem. Soc.*, 1953, 3042.
37 L. H. Welsh, *J. Amer. Chem. Soc.*, 1941, **63**, 3276.
38 A. Mangini, *Gazzetta*, 1936, **66**, 675.
39 K. H. Menzel and R. Puetter, Belgium P. 643,807 (*Chem. Abs.*, 1965, **63**, 4440f).
40 F. G. Pope and J. M. Hird, *J. Chem. Soc.*, 1901, **79**, 1141.
41 S. G. P. Plant and R. J. Rosser, *J. Chem. Soc.*, 1928, 2454.
42 J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1220.
43 D. Dal Monte, A. Mangini, and R. Passerini, *Gazzetta*, 1956, **86**, 797.
44 H. G. Garg and S. S. Joshi, *J. Org. Chem.*, 1961, **26**, 946.
45 I. L. Finar and R. J. Hurlock, *J. Chem. Soc.*, 1957, 3024; see ref. 7 for synthetic method.
46 L. Maaskant, *Rec. Trav. chim.*, 1937, **56**, 211.
47 C. Ainsworth, *Org. Synth.*, 1963, Coll. Vol. IV, 536.
48 R. G. Micetich, *Canad. J. Chem.*, 1970, **48**, 2006.