SYNTHESIS OF DIMETHYLPYRAZOLO[1,2-*a*]BENZOTRIAZOLES AND OF METHYLPYRAZOLO[1,2-*a*]QUINOXALINES BY CYCLIZATION OF 3,5-DIMETHYL-1-(2-NITRENOPHENYL)PYRAZOLES §

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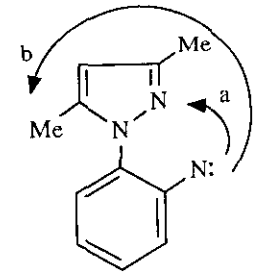
Abstract-The thermal and photochemical decomposition of a series of 5-substituted 1-(2-azidophenyl)-3,5-dimethylpyrazoles has been examined under a homogeneous set of conditions. Cyclization to pyrazolo[1,2-*a*]benzotriazole (*via* singlet nitrene) is an efficient process except when the phenyl substituent induces intersystem crossing to the azide triplet or compensates for its electrophilicity. On the contrary, cyclization to pyrazolo[1,2-*a*]quinoxaline (*via* triplet nitrene) is not a preparatively useful process, due to competition with dimerization to the azo derivatives and reduction to aminophenylpyrazoles.

Aromatic nitrenes, usually generated either by decomposition of azides or by deoxygenation of nitro compounds, are convenient intermediates for the synthesis of nitrogen heterocycles.[1] A typical example is the preparation of carbazoles (*via* singlet nitrene) from 2-azidobiphenyls.[2] When 2-azido-2'-methylbiphenyl is used as the starting material, phenanthridine (*via* triplet nitrene) is obtained along with methylcarbazole (through the singlet pathway).[3]

A related reaction, first reported by Lynch and Hung in 1965,[4] is the deoxygenative cyclization of 1-(2-nitrophenyl)pyrazole to pyrazolo[1,2-*a*]benzotriazole. Some years later, McRobbie and coll.[5] observed that 3,5-dimethyl-1-(2-nitrenophenyl)pyrazole appears to be the archetype of compounds having an attractive site for attack by the singlet (viz the nitrogen atom in position 2) or by the triplet (the methyl group in position 5) nitrene (see formula **1**, paths a and b). The first reaction leads to a pyrazolobenzotriazole, the latter one to a pyrazoloquinoxaline.



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The above authors showed[5] that by appropriately chosing the mode of nitrene generation the ratio of singlet vs triplet derived products could be largely changed, and furthermore that substituents on the aromatic ring could largely affect the nitrene reactivity.

Although the general rationalization offered by McRobbie and coll. is on the whole appropriate, an attempt to reproduce some of their results gave different results in our hands.[6] Therefore we deemed worthwhile to carry out a systematic survey of the reactivity of 3,5-dimethyl-1-(2-nitreno-5-substituted phenyl)pyrazoles generated

§ Dedicated to Professor Rolf Huisgen on the occasion of his 75th birthday.

from the corresponding azides under various conditions (see Scheme 2). In the series (**1a-g**) the substituent in *para* to the nitrene is expected to exert a large effect on its electrophilic or radicalic nature, and in nitrene (**1h**) the second nitro group on the pyrazole ring is expected to change the nucleophilicity of the pyrazole moiety. The decomposition of the azides (**2a-h**) was examined under the following conditions:

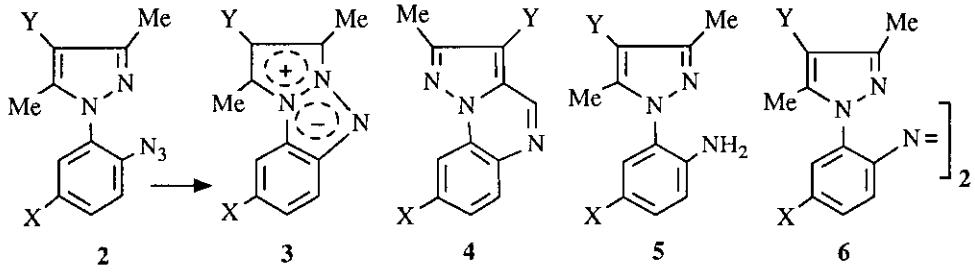
a. thermal decomposition of the neat material at a temperature such that most of the azide is decomposed in some minutes ;

b. thermal decomposition in solution under the same conditions as above;

c. photolysis at room temperature; in some cases the medium and temperature effects have also been investigated;

d. triplet photosensitized decomposition at room temperature.

The products obtained from preparative scale photolysis (both direct and sensitized) were separated by column chromatography (Table 3). These are: the pyrazolobenzotriazoles (**3**), the pyrazoloquinoxalines (**4**), the aminophenylpyrazoles (**5**), and the pyrazolylazobenzenes (**6**) (Scheme 1). Structure assignement follows from their spectroscopic and analytic properties (see Experimental).



Scheme 1

In order to be able to draw a quantitative picture of the two competitive nitrene attacks and of the substituent effect, separate small scale experiments under the above conditions were carried out using $4x10^{-3}$M solutions of the azides. These gave the products reported in Table 1 (yields determined by hplc; >95% of the products is recovered when they are subjected to the same conditions).

The general trends emerging from this work are as follows:

-- the pyrazolobenzotriazoles (**3**) are obtained in fair to excellent yield both by thermolysis and by photolysis of the azides (**2a, b, e-h**) (however, the yield of **3h** is satisfactory only by thermal fragmentation of the azide). Under these conditions, the singlet nitrene is the reacting species, and arises either from the ground state or from the singlet excited state of the azide. Intramolecular nucleophilic trapping is very effective, and relatively good yields of the heteropentalenes (**3**) are obtained even under drastic conditions, such as heating of the neat material, in contrast to what observed with phenylazide, where polymerization predominates under most conditions.[1,7]

Differently from earlier claims, an activating electron-withdrawing substituent on the aromatic ring is not a prerequisite. However, an electron donating substituent in *para* completely suppresses the electrophilic cyclization. The effect is stronger than observed for the intermolecular trapping, since it is known[8] that singlet *p*-methoxyphenylnitrene is trapped by secondary amines, although less efficiently than the parent derivative,

while *p*-dimethylaminophenylnitrene is not trapped at all.

In general, thermolysis in an inert solvent appears to be the method of choice for the synthesis of products (**3**), giving somewhat better yields than photolysis at room temperature. In particular, in the case of the nitro derivatives (**2g-h**), the yield of **3** by photodecomposition is low. This is due to an enhancement of the inter system crossing from the singlet excited state to the triplet state of the azide induced by the substituent, as it is the rule with nitroaromatics, which leads to direct population of the triplet nitrene. Furthermore, in the case of (**1h**), electrophilic cyclization is slowed down by the second nitro group on the pyrazole ring. Both limitations are overcome when the azide is thermally decomposed, and thus singlet nitrene with excess vibrational energy is produced.

-- the azo derivatives (**6**) are main products under some conditions. Surprisingly, previous workers reported that no azo derivatives were formed from nitrenes of this type.[5] The present results show that nitrenes (**1**) are quite similar to phenylnitrene, and dimerization to products (**6**) is the main path when the triplet path is operative, either because of spontaneous intersystem crossing from singlet to triplet azide (e.g. in the case of **2g**, direct irradiation), or triplet azides are directly reached by sensitization (condition d), or the electrophilic cyclization of singlet nitrene is hindered (**2c, d, h**) and it rather crosses down to triplet nitrene.

On the other hand, when triplet nitrene with excess vibrational energy is generated, the yield of the azo compounds are strongly decreased in favour of products (**4**) and (**5**) (see direct irradiation of **2c** at 80°C and sensitized irradiation of **2h** at 50°C).

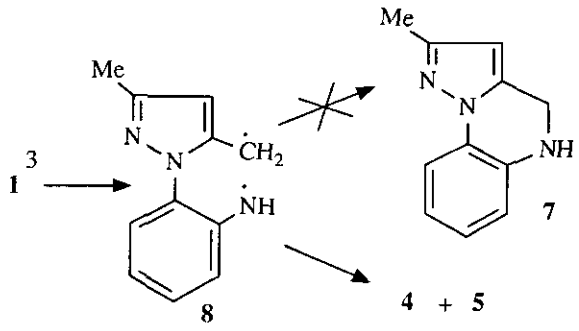
-- cyclization to the quinoxalines (**4**) is not a preparatively useful procedure. Triplet arylnitrenes generally have no marked radical character, and intermediates (**1**) make no exception even if intramolecular hydrogen abstraction would be available. In the present molecules, both the pyrazole ring in *ortho* and the substituent in *para* further stabilizes the triplet nitrene through delocalization, and thus slow down hydrogen abstraction. As remarked above, a considerable barrier is involved in this reaction, and it considerably benefits from a temperature enhancement. A peculiar characteristic is that in most cases the yields of products (**4**) and (**5**) are quite similar, and they grow in a parallel way when the temperature is enhanced (with some exception, e.g. with the methoxy derivative (**2c**) the yield of the quinoxaline (**4c**) obtained by thermolysis is fair, and it is larger than that of the amine). This, together with the fact that no dihydropyrazoloquinoxaline (**7**) was detected in this work or in previous investigations[5] leads one to suspect that intramolecular hydrogen abstraction is the first step, but the biradical (**8**) disproportionates to a 1 to 1 mixture of **4** and **5** rather than undergoing cyclization (Scheme 2). That intermolecular hydrogen abstraction is not important is also indicated by the fact that the **5** to **4** ratio is not enhanced upon photolysis of the azide in a better hydrogen donating solvent such as cyclohexane. However, the mechanism is somewhat more complicated, as shown by the considerable effect that the solvent polarity has on the products distribution (see yields of compounds **4**, **5**, and **6** from **2c** and **2d**; benzene gives the same results as cyclohexane). This probably is due to a change in the preferred conformation in the nitrene with the polarity, making the methyl group more or less available to the radicalic attack.

In conclusion, the present investigations shows that decomposition of the azidophenylpyrazoles (**2**), in particular thermolysis in an inert solvent, is a viable method for the synthesis of the pyrazolobenzotriazoles (**3**) for all the derivatives except those bearing a strong electron-donating susbtituent, while the synthesis of the pyrazoloquinoxalines (**4**) by this way is generally unsatisfactory, and at any rate leads to a mixture with near to equimolecular amounts of the corresponding amines (**5**).

Table 1. Products obtained from the decomposition of the azides (**2**).

Azide	X, Y	Conditions	Time min	Conversion (%)	Products(%) **3**	**4**	**5**	**6**
2a	H, H	a, 143°C	30	35	58	-	tr	-
		b, MeCN, 143°C	30	35	90	-	-	-
		c, MeCN, hν	5	60	90	-	-	-
		d, MeCN, hν[v]	40	90	-	13	12	54
2b	Me, H	a, 143°C	30	86	20	2	2	-
		b, MeCN, 143°C	30	87	59	15	5	tr
		c, MeCN, hν	5	85	43	1	tr	7
		d, MeCN, hν[w]	15	95	-	5	4	34
2c	OMe, H	a, 143°C	10	54	-	27	30	tr
		b, MeCN, 143°C	10	55	-	53	32	3
		c, MeCN, hν	5	85	-	7	10	62
		c, C_6H_{12}, hν	5	82	-	17	16	17
		c, MeCN, 80°C, hν	5	90	-	39	43	5
		d, MeCN, hν[w]	15	68	-	14	15	48
2d	NMe_2, H	a, 143°C	5	98	-	16	22	3
		b, MeCN, 143°C	5	95	-	20	22	3
		c, MeCN, hν	5	98	-	6	10	8
		c, C_6H_{12}, hν	5	95	-	21	14	24
		d, MeCN, hν[w]	15	95	-	6	19	23
2e	Cl, H	a, 143°C	30	43	18	5	1	4
		b, MeCN, 143°C	30	47	74	-	2	5
		c, MeCN, hν	5	50	60	-	-	7
		d, MeCN, hν[w]	60	80	tr	11	3	24
2f	CF_3, H	a, 170°C	6	29	92	tr	tr	tr
		b, MeCN, 170°C	6	30	94	-	-	-
		c, MeCN, hν	5	68	70	tr	tr	tr
		c, MeCN, 80°C, hν	5	68	74	-	-	-
		d, MeCN, hν[x]	30	76	7	24	24	20
2g	NO_2, H	a, 143°C	30	73	66	-	tr	tr
		b, MeCN, 143°C	30	40	90	-	-	-
		c, MeCN, hν	5	96	47	-	3	26
		d, MeCN, hν[y]	30	99	7	4	10	40
2h	NO_2, NO_2	a, 165°C	30	88	37	-	5	tr
		b, MeCN, 165°C	30	75	90	-	5	-
		c, MeCN, hν	5	86	12	-	5	82
		d, MeCN, hν[z]	25	90	-	6	12	56
		d, MeCN, 50°C, hν[z]	25	90	tr	13	22	25

v. PhAc 25%. w. PhAc 2%. x. PhAc 5%. y. Ph_2CO $8x10^{-2}$M. z. Thioxanthone $1.5x10^{-2}$ M



Scheme 2

EXPERIMENTAL

The key spectroscopic characteristics of new products are reported in Table 2. Nmr spectra were measured by means of a Brucker 300 instrument, and mass spectra by means of a Finnigan MAT instrument.

Synthesis of the azides (2). The azides (**2a**, **2d**, and **2e**) were prepared and purified as previously reported.[5,9]

1-(2-Azido-5-methylphenyl)-3,5-dimethylpyrazole (2b). To a stirred solution of 3-fluoro-4-nitrotoluene (3.1 g, 20 mmol) in DMF (100 ml) Na_2CO_3 (2.2g, 22mmol) and hydrazine hydrate (98%, 1.5 ml, 30 mmol) were added at room temperature, and stirring was continued for 6 h. Upon dilution with 150 ml of H_2O, an orange precipitate (2.2 g) was obtained. Extraction of the filtrate with 3x50 ml of Et_2O afforded further solid (1 g). The combined solids were crystallized from cyclohexane to give the 5-methyl-2-nitrophenylhydrazine (2.5 g, 75% yield) as soft orange needles, mp 126.5-127.5°C. Anal. Calcd for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.50; H, 5.47; N, 25.00. 1.67 g (10 mmol) of the above product was refluxed with $MeCOCH_2COMe$ (1.2 ml, 12 mmol) in ethanol (20 ml) containing 2 drops of conc. HCl for 4 h. Removal of the solvent and recrystallization from *n*-hexane gave 1-(5-methyl-2-nitrophenyl)-3,5-dimethylpyrazole (2.15 g, 93% yield) as pale yellow prisms mp 100-101°C. Anal. Calcd for $C_{12}H_{13}N_3O_2$: C, 62.32; H, 5.67; N, 18.17. Found: C, 62.40; H, 5.67; N, 18.22. By the usual procedure[9] catalytic hydrogenation at room temperature gave **5b** (colorless prisms, 65% yield), and diazotization in $AcOH-H_2O-HBF_4$ and reaction with NaN_3 gave the title compound (92%).

1-(2-Azido-5-methoxyphenyl)-3,5-dimethylpyrazole (2c). Starting from the 1-(5-methoxy-2-nitrophenyl)-3,5-dimethylpyrazole[5] the amine (**5c**) (colorless leaves, 79% yield) and the title compound (86%) were prepared as above.[5]

1-(2-Azido-5-trifluoromethylphenyl)-3,5-dimethylpyrazole (2f). A solution of 2-nitro-5-trifluoromethylphenylhydrazine[10] (6.63 g, 30 mmol) and $MeCOCH_2COMe$ (3.4 ml, 33 mmol) in 50 ml of ethanol containing 3 drops of conc. HCl was refluxed for 10 min. Removal of the solvent and recrystallization of the crude product from *n*-hexane gave 1-(2-nitro-5-trifluoromethylphenyl)-3,5-dimethylpyrazole as creamy cristals, mp 58.5-59°C (7.2 g, 85%). Anal. Calcd for $C_{12}H_{10}F_3N_3O_2$: C, 50.52; H, 3.51; N, 14.73. Found: C, 50.60; H, 3.51; N, 14.70. By the usual procedure,[9] catalytic reduction gave the amine (**5f**) (colorless needles, 90% yield). This was diazotized in $AcOH-HBF_4$ and treated with NaN_3 as above. Neutralization with solid $NaHCO_3$, extraction with chloroform, driying, and removal of the solvent gave an oil which was purified by column chromatography on alumina eluting with benzene to yield **2f** as a colourless viscous oil (87%, after drying

under vacuum,1 torr, 80°C; 97% hplc purity).

1-(2-Azido-5-nitrophenyl)-3,5-dimethylpyrazole (2g) and 1-(2-Azido-5-nitrophenyl)-3,5-dimethyl-4-nitro pyrazole (2h). To a boiling solution of 1-(2-aminophenyl)-3,5-dimethylpyrazole[5] (7.48 g, 40 mmol) in dry benzene (60 ml) Ac_2O (97%, 4.2 ml, 44 mmol) was gradually added and refluxing was continued for 30 min. Removal of the solvent gave the anilide as a a colorless solid (8.9 g, 97%, mp 101-103°C), used as such; recrystallization from cyclohexane gave mp 102.5-103.5°C. Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 68.27; H, 6.49; N, 18.30. This material (6.87 g, 30 mmol) was powdered and added while stirring to conc. H_2SO_4 (30 ml) maintaining the temperature at 20°C. The solution was cooled at -5°C, and a mixture of conc. H_2SO_4 (15 ml) and HNO_3 (90%, 15 ml) was added dropwise in 25 min. After a further 1 h stirring at -5°C, the solution was poured in ice (200 g), diluted with H_2O (1 l) and neutralized with solid $NaHCO_3$. The precipitate was filtered, stirred with 500 ml of water and filtered again to give 7.87 g of a creamy solid, mp 146-175°C, shown by hplc to be a mixture of two products. As separation at this stage was difficult, the mixture was dissolved in conc. H_2SO_4 (15 ml), heated at 110°C for 5 min and poured in ice cold water (500 ml). Neutralization with solid $NaHCO_3$ and filtration gave a yellow solid (6.4 g) which was chromatographed on a silica gel column eluting with benzene - ethyl acetate 8:2 mixture to yield the amines (**5h**) (1.8 g, 22%) and (**5g**) (4.4 g, 63%). The azides (**2g**) (94%) and (**2h**) (95%) were prepared as above.

CAUTION. The azides (**2f,g,h**) and their derivatives are strongly irritating.

Preparative photolysis of the azides (2). To anhydrous acetonitrile (300 ml) deaerated by boiling and cooled under a stream of argon was added the azide (**2**) (1.2 mmol), and after 15 min of additional flushing, the resulting solution was irradiated under one of the following conditions (see Table 3): 1. in an immersion well apparatus through a quartz jacket by means of a low-pressure mercury arc (Helios Italquartz 15W); 2. in an immersion well apparatus through a Pyrex jacket by means of a medium pressure mercury arc (Helios Italquartz 125W); 3. in a Pyrex Erlenmeyer flask by means of an external focalized high pressure mercury arc (Osram 200W). In every case an argon stream was maintained during irradiation. In cases 1 and 2 the temperature was 17°C, while under condition 3 the solution was refluxed during irradiation. After the time period reported in Table 3 the reaction mixture was evaporated at reduced pressure at room temperature, and the residue was chromatographed on a silica gel column eluting with benzene-ethyl acetate 9:1 to 7:3 mixtures. The highly insoluble azo compounds (**6g,h**) in part precipitated out and were treated separatedly. The characterization of products (**3a,e**, **4a,c,d,e**, **5a,d,e**, **6a,e**) has been previously reported.[5,9]

Small-scale experiments (Table 1). Photodecompositions (conditions c and d). Solutions (2 ml) of the azides (**2**) ($4x10^{-3}$M) in quartz spectrophotometric couvettes were deaerated by flushing with argon for 30 min and irradiated while stirring by means of a focalized high pressure mercury arc (Osram 200W) through a Pyrex filter for condition d (except than with **2g**), with no filter in the other cases. The photolyzed solutions were diluted, and analyzed by hplc through a Waters Microbondapack C-18 column (30 cm long, 3.9 mm i.d.) isocratically eluting with MeCN-H_2O 85:15 to 7:3 mixtures after addition of an internal standard, with optical detection. In the experiments with PhAc as the sensitizer, this was distilled away at room temperature under vacuum before analyzing. *Thermolysis of the neat material (condition a).* A sealed capillary tube containing samples (1 to 2 mg) of the azide was immersed in a pre-heated thermostatted bath. Afterwards the tubes were triturated in MeCN, and the solution analyzed as above. *Thermolysis in solution.* Pyrex tubes containing

solutions (2 ml) of the azides ($4x10^{-3}M$) were sealed and immersed in a pre-heated thermostatted bath. Afterwards the solutions were analyzed as above.

Table 2a. Main data about compounds **2-6**.

Compound	mp(°C)		Nmr (δ in $CDCl_3$)				
		Me	H-4	H-3'	H-4'	H-6'	
2b	64-65[a]	2.15,2.3,2.35	6.0	7.1	7.25	7.15	
2c	69-70[b]	2.15,2.3,3.7	6.05	7.15	7.0	6.9	
2f	oil	2.15,2.35	6.05	7.35	7.7	7.62	
2g	82-83[c]	2.15,2.3	6.05	7.3	8.3	8.2	
2h	153-156[d]	2.5,2.6	-	7.5	8.5	8.3	
		Me	H-2	H-6	H-7	H-8	
3b	101-102[b]	2.45,2.55,2.75	6.25	7.35	7.15	7.45	
3f	153-154[e]	2.6,2.8	6.4	7.4	7.55	7.85	
3g	238[f]	2.6,2.8	6.4	7.25	8.25	8.5	
3h	255-260[g]	3.0,3.25	-	7.45	8.35	8.7	
		Me	H-3	H-4	H-6	H-7	H-9
4b	93-94[h]	2.6	6.65	8.9	7.95	7.35	8.25
4f	85-86[c]	2.6	6.75	9.05	8.2	7.75	8.8
4g	205-208[h]	2.65	6.8	9.1	8.2	8.35	9.35
4h	205-206[d]	2.95	-	9.85	8.4	8.55	9.45
		Me	H-4	H-3'	H-4'	H-6'	NH_2
5b	75-77[c]	2.15,2.25,2.3	6.0	6.75	7.0	6.9	3.8
5c	103-104[e]	2.2,2.3,3.7	6.0	6.8	6.85	6.7	3.65
5f	83-84[c]	2.2,2.3	6.0	7.35	7.4	7.35	4.35
5g	176-178[g]	2.25,2.35	6.1	7.1	8.1	8.0	4.95
5h	250-251[g]	2.5,2.55	-	7.1	8.2	8.1	6.25
		Me	H-4'	H-3	H-5	H-6	
6b	209-210[e]	2.35,2.45	6.05	7.4	7.2	7.4	
6c	211-212[g]	2.0,2.35,3.9	6.05	7.05	6.95	7.5	
6d	>300[i]		6.0	6.75	6.7	7.5	
6f	224-225[e]	2.05,2.35	6.1	7.9	7.55	7.7	
6g	287-288[j]	2.1,2.4	6.1	8.5	8.3	7.6	
6h	>300[k l]		-	8.7	8.6	7.6	

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a. from *n*-pentane. b. from light petroleum ether. c. from *n*-hexane. d. from benzene. e. from cyclohexane. f. from ethyl acetate. g. from ethanol. h. chromatographic purification. i. from acetic acid. j. from chloroform. k.

Table 2b. Elemental analyses of compounds (**2-6**).

Compound	Formula	Ms (M^+)	Analysis Calcd(Found)		
			C	H	N
2b	$C_{12}H_{13}N_5$		63.42(63.81)	5.77(5.76)	30.82(30.92)
2c	$C_{12}H_{13}N_5O$		59.25(58.98)	5.39(5.28)	28.79(28.78)
2f	$C_{12}H_{10}N_5F_3$	281	51.24(51.58)	3.55(3.71)	24.92(25.15)
2g	$C_{11}H_{10}N_6O_2$		51.16(51.34)	3.90(3.85)	32.55(32.47)
2h	$C_{11}H_9N_7O_4$	303	43.56(43.68)	2.99(3.09)	32.33(32.48)
3b	$C_{12}H_{13}N_3$	187	72.33(72.05)	6.57(6.56)	21.09(20.88)
3f	$C_{12}H_{10}N_3F_3$	253	56.91(56.75)	3.98(4.01)	16.59(16.67)
3g	$C_{11}H_{10}N_4O_2$	230	57.38(57.62)	4.38(4.36)	24.34(24.26)
3h	$C_{11}H_9N_5O_4$	275	48.00(48.12)	3.30(3.32)	25.45(25.38)
4b	$C_{12}H_{11}N_3$	197	73.07(72.93)	5.62(5.68)	21.31(21.14)
4f	$C_{12}H_8N_3F_3$	251	57.37(57.48)	3.21(3.29)	16.73(16.81)
4g	$C_{11}H_8N_4O_2$	228	57.89(57.64)	3.53(3.58)	24.55(24.61)
4h	$C_{11}H_7N_5O_4$	273	48.35(48.63)	2.58(2.61)	25.64(25.54)
5b	$C_{12}H_{15}N_3$	201	71.61(71.77)	7.51(7.64)	20.88(21.10)
5c	$C_{12}H_{15}N_3O$	217	66.34(66.39)	6.96(6.92)	19.34(19.36)
5f	$C_{12}H_{12}N_3F_3$	255	56.47(56.60)	4.70(4.81)	16.47(16.58)
5g	$C_{11}H_{12}N_4O_2$	232	56.89(57.01)	5.21(5.34)	24.13(24.21)
5h	$C_{11}H_{11}N_5O_4$	277	47.65(47.39)	4.00(4.08)	25.26(25.31)
6b	$C_{24}H_{26}N_6$	398	72.33(72.38)	6.57(6.65)	21.09(20.87)
6c	$C_{24}H_{26}N_6O_2$	430	66.95(66.78)	6.09(6.05)	19.52(19.44)
6d	$C_{26}H_{32}N_8$	456	68.39(68.51)	7.06(7.12)	24.54(24.36)
6f	$C_{24}H_{20}N_6F_6$	506	56.91(56.71)	3.98(4.05)	16.59(16.65)
6g	$C_{22}H_{20}N_8O_4$	460	57.38(57.56)	4.38(4.31)	24.34(24.61)
6h	$C_{22}H_{18}N_{10}O_8$	550	48.00(47.92)	3.30(3.41)	25.45(25.56)

Table 3. Preparative photolysis of the azides (**2**).

Azide	Condition (see text)	Time min	Conversion (%)	Products (% Yield) **3**	**4**	**5**	**6**
2a	1	30	70	58	-	-	-
	2[a]	90	50	-	20	10	57
2b	1	40	95	45	1	-	6
	2[a]	90	95	-	14	10	36
2c	2	40	96	-	6	3	71
2d	2[b]	40	90	-	19	8	43
2e	1	40	84	53	-	-	5
	2[a]	90	95	tr	10	2	27
2f	1	130	95	79	-	-	-
	2[a]	120	98	4	20	19	20
2g	2	10	92	41	-	-	23
	1[c]	60	90	3	5	8	40
2h	2	25	96	12	-	2	63
	3[d]	300	90	2	24	20	-

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a. in MeCN in the presence of 2% PhAc. b. in benzene. c. in MeCN in the presence of $8x10^{-2}$M Ph_2CO. d. in MeCN in the presence of $1.5x10^{-2}$M thioxanthone.

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