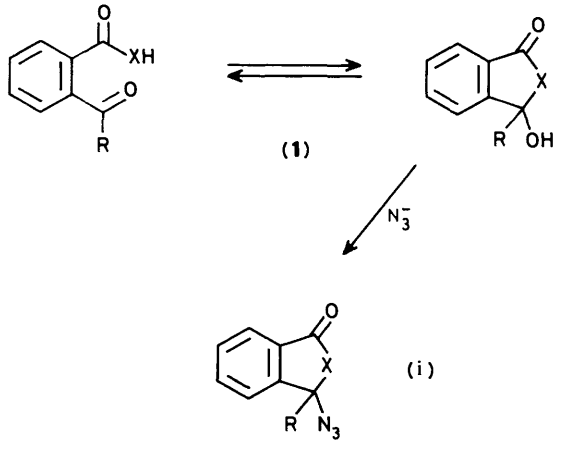
Benzylic Azide Functionalization of Tautomeric *o*-Acyl-benzoic Acid, -benzamide, and -nicotinic Acid Derivatives, and Thermal Decomposition of the Derived Azides[1]

Hisato Takeuchi and Shoji Eguchi *
Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

A series of benzylic azido compounds were prepared by the reactions of *o*-acyl-benzoic acids and -benzamides and pyridine analogues with sodium azide, diphenylphosphoryl azide, and trimethylsilyl azide. Thermal decomposition of the derived benzylic azides afforded three types of rearrangement products. The selectivity of rearrangement depended on the migratory aptitude of substituents and on stereoelectronic factors.

In natural product chemistry there are many ring–chain tautomers which exist in both forms, as exemplified by many saccharides. The structural and physical chemistry of such systems have been studied,[2] but their synthetic application seems limited.[3] However, if an azido group could be introduced into the ring form of a ring–chain tautomer, nitrogen heterocyclic compounds could well be derived easily by thermal or photolytic decomposition.[4–6] We considered *o*-acyl-benzoic acid and -benzamide derivatives (**1**), as simple ring–chain tautomers, suitable for such a study, because (**1**) exists primarily in the ring form and the benzylic hydroxy group would be expected to be reactive towards substitution with azide anion [equation (i)].



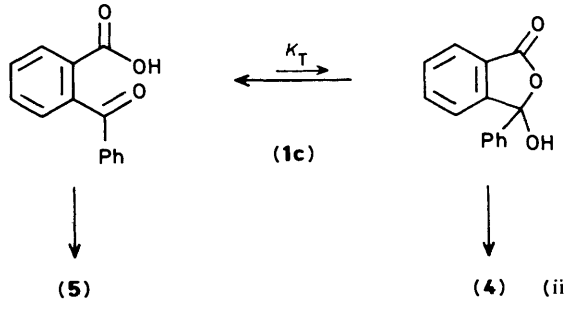
X = O: (**2**) R = H (**3**) R = Me (**4**) R = Ph
X = NMe (**6**) R = H (**8**) R = Me (**9**) R = Ph
X = NPh (**10**) R = Me (**11**) R = Ph

In this report, we describe the azide functionalization of compounds (**1**) and the thermal decomposition of the derived azides.

Results and Discussion

Azide Functionalization of o*-Acyl-benzoic Acids, -benzamides, and -nicotinic Acid Derivatives.*—*o*-Acetyl-benzoic acids and -benzamides (**1**) were prepared from phthalic anhydride and *N*-methyl- and *N*-phenyl-phthalimides by Grignard reaction or reduction with $NaBH_4$.[7]

The hydroxy group of the ring form of (**1**) was substituted with an azido group by four methods (Table 1). Methods A—C are procedures known to convert carboxylic acids into the corresponding acyl azides. Method D, with trimethylsilyl azide, followed the procedure of Kraus *et al.*[3a] When the substituents on (**1**) were small (R = H or Me), method C [diphenylphosphoryl azide (DPPA) at room temperature] yielded azido compounds (**2**), (**3**), and (**6**) in high yields (Table 1, entries 2, 4, and 7). The mild conditions of method C did not give good results with R = Ph, because of steric hindrance. On the other hand, method A or B afforded azido compounds in good yields even for compounds (**1**) with bulky substituents (Table 1, entries 5, 11, and 14). In the case of *o*-benzoylbenzoic acid (**1c**), the ring–chain equilibrium constant K_T is 0.07,[2] indicating the presence of only a very small amount of the ring form [equation (ii)]. However treatment of (**1c**) by method A afforded the azido lactone (**4**) in 91% yield *via* the ring form.

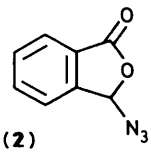
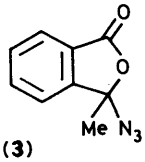
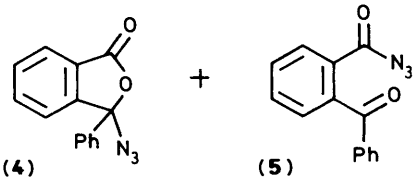
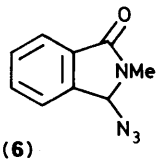
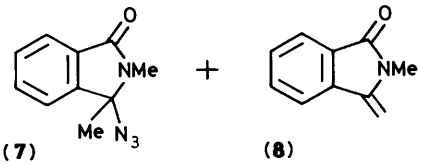
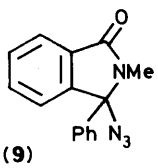
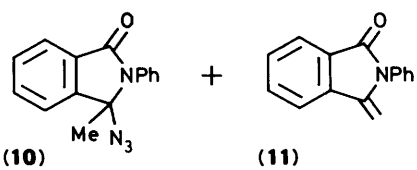
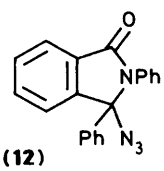


In the reaction of *o*-acetylbenzamide (**1e**) by method C, dehydration to (**8**) predominated over the desired azide functionalization (Table 1, entry 8). With method D, however, this side reaction was largely suppressed and the yield of azide (**7**) was improved to 70% (Table 1, entry 9).

We also investigated the azide functionalization of the pyridine analogues (**13**) and (**15**). By the procedure of Nagano *et al.*,[8] compounds (**13**) and (**15**) were prepared from nicotinic acid *N*-oxide. Their reactions were performed by method C, with dimethylformamide (DMF) as solvent because of a solubility problem. The azido compounds (**14**) and (**16**) were obtained in 94 and 99% yields, respectively [equations (iii) and (iv)].

Thermal Decomposition of Azido Compounds.—Thermal decomposition of these azides could in principle afford three types of rearrangement product [(**17**)—(**19**); equation (v)]. In route (*a*) participation of the fused benzene or pyridine ring followed by rearrangement affords (**17**), in (*b*) rearrangement of

Table 1. Azide functionalization reactions

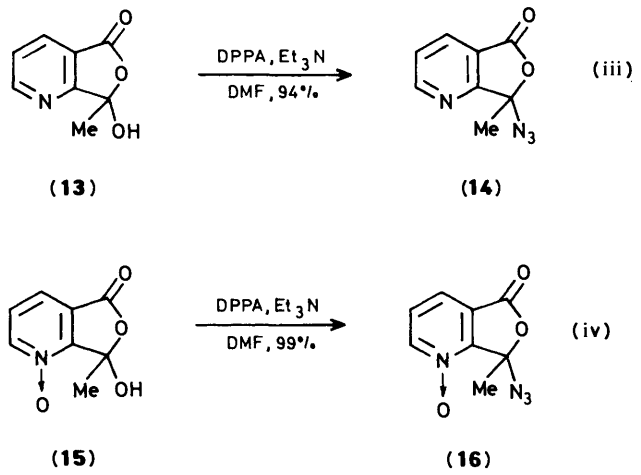
Entry	Substrate	X	R	Products	Method[a]	Yield (%)
1	(1a)	O	H	 (2)	A	84
2	(1a)	O	H		C	92
3	(1b)	O	Me	 (3)	A	79
4	(1b)	O	Me		C	100
5	(1c)	O	Ph	 (4) + (5)	A	91[b]
6	(1c)	O	Ph		C	28[b]
7	(1d)	NMe	H	 (6)	C	74
8	(1e)	NMe	Me	 (7) + (8)	C	18 + 36
9	(1e)	NMe	Me		D	70 + 11
10	(1f)	NMe	Ph	 (9)	A	30
11	(1f)	NMe	Ph		B	75
12	(1f)	NMe	Ph		C	No reaction
13	(1g)	NPh	Me	 (10) + (11)	D[c]	33 + 52
14	(1h)	NPh	Ph	 (12)	B	99

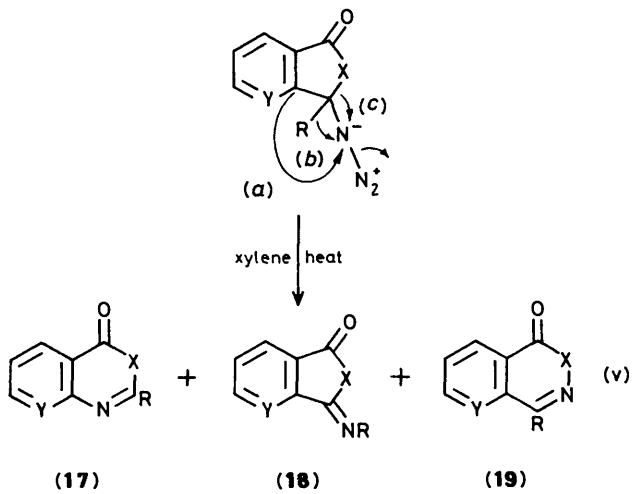
[a] A: i, $SOCl_2$, benzene; ii, NaN_3, H_2O, benzene, phase-transfer catalyst. B: i, $SOCl_2$, benzene; ii, $Bu_4N^+N_3^-$, MeCN. C: DPPA, Et_3N, benzene. D: Me_3SiN_3, BF_3·Et_2O, CH_2Cl_2, −78 °C (see Experimental section). [b] Yield of isolated (4); (5) was not isolated. [c] Solvent CH_2Cl_2–tetrahydrofuran; −78 °C; room temp.

Table 2. Azide thermolysis

Entry	Azide	R	Yields (%) (17)	(18)	(19)
1	(2)	H		73	
2	(3)	Me	62		
3	(4)	Ph	38	51	
4	(6)	H		65	
5	(9)	Ph	33	28	
6	(12)	Ph	53	30[a]	
7	(14)	Me	Trace		35
8	(16)	Me			35

[a] As a mixture with (12) (see Experimental section).

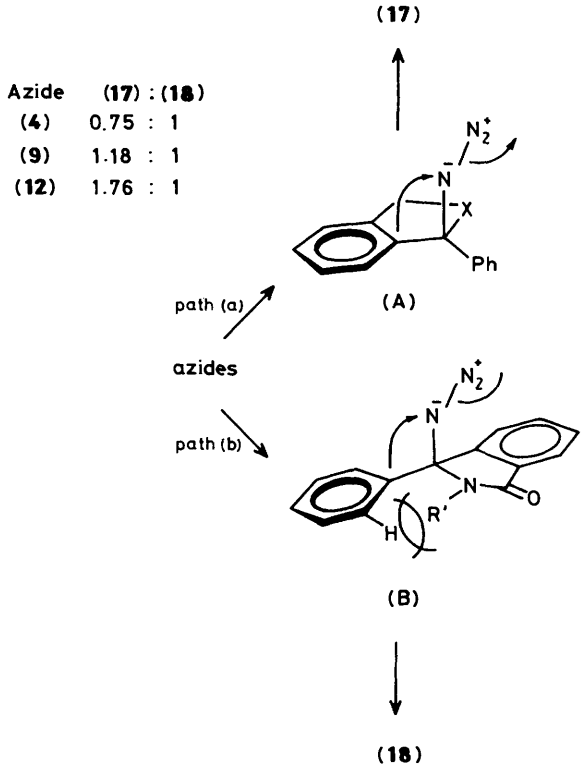




substituent R gives (**18**), and in (*c*) participation of X leads to (**19**).

Normal alkyl azides undergo thermolysis generally at temperatures in excess of 180 °C.[5a] However, the present azido compounds were decomposed at lower temperatures, *e.g.* in refluxing xylene (b.p. 138.5—141.5 °C); this suggested neighbouring group participation. Thermolysis of α-azido sulphides has been reported to proceed readily at 120 °C *via* sulphur atom participation.[5d]

The present thermolysis results are summarized in Table 2. The regioselectivity depended principally on the migratory

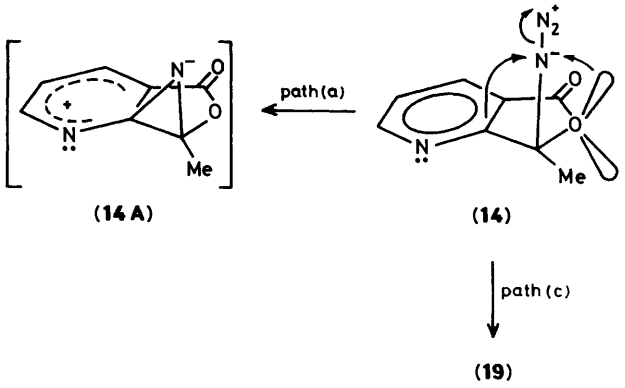


Scheme 1.

aptitude of R (H > Ph > Me). For R = H [(**2**) and (**6**)] products (**18**) were obtained exclusively by migration of H. For R = Me [(**3**)], the product (**17**) was produced selectively by migration of the fused benzene ring. For R = Ph, products (**17**) and (**18**) were both formed, by competing migration of the phenyl substituent and the fused benzene ring [(**4**), (**9**), and (**12**)]. The ratio of (**17**) to (**18**) seems to be controlled by steric factors (*i.e.* steric effects or stereoelectronic factors). The ratio (**17**):(**18**) increases as X becomes more bulky (O < NMe < NPh; Scheme 1). This can be rationalized as follows: in path (a) to (**17**), aryl π-participation in the decomposition of the azide group is feasible [(A) in Scheme 1], whereas in path (b) to (**18**), this is inhibited by steric hindrance between the phenyl group and R′ [(B) in Scheme 1]. Thus phenyl migration in (**12**) (R′ = Ph) could be largely suppressed, as observed.

In the cases of the pyridine derivatives (**14**) and (**16**) (X = O, Y = N, or N→O, R = Me), the lactone oxygen-rearranged product (**19**) was obtained selectively by thermolysis. This result was in contrast with the reaction of (**3**), which gave the fused benzene ring rearranged product (**17**) exclusively. If the π-orbital of the fused pyridine ring participates, an intermediate like (**14A**) would be generated, with nitrogen loss. However the electron-withdrawing nature of the pyridine nitrogen atom disfavours such participation. The pyridine ring shifted product, (**17**) (X = NMe, Y = N, R = Me) is formed only in trace amounts, and is unstable on t.l.c. (silica gel). Thus only the lactone oxygen-participation product (**19**) was obtained (Scheme 2). On the other hand, *C*-nitration of the pyridine *N*-oxide ring is known to be easier than that of pyridine (pyridinium ring under acidic conditions), owing to back-donation of the lone pair on the oxygen atom.[9] Although (**16**) has a pyridine *N*-oxide ring, such a directive stabilization resonance effect on the regioselectivity of the ring expansion was not reflected in the product distribution.

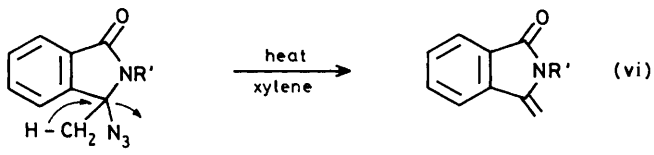
Thermal decomposition of compounds (**7**) and (**10**) afforded



(14A) (14) (19)

Scheme 2.

only the elimination products, (**8**) and (**11**), respectively. Because of the presence of a β-hydrogen atom, and the stability of the enamides (**8**) and (**11**), the elimination of hydrazoic acid was preferred to decomposition of the azido group [equation (vi)].



(vi)

(**7**) R' = Me (**8**) 81%
(**10**) R' = Ph (**11**) 72%

In summary, benzylic azide functionalization of *o*-acylbenzoic acid, -benzamide, and -nicotinic acid derivatives proceeds smoothly *via* the appropriate tautomer. Thermal decomposition of the derived azides occurs at relatively low temperatures to afford three types of rearrangement product. The selectivity of rearrangement depends on the substituents and on steric effects. Among the products observed, structures of types (**17**) and (**18**) occur in some synthetic medicines [10] and synthetic dyes.[11] This ready azide functionalization reaction could provide an efficient route to interesting nitrogen heterocycles.

Experimental

M.p.s were determined with a Yanagimoto micro apparatus. Elemental analyses were performed with a Perkin-Elmer 240B elemental analyzer. ^{1}H N.m.r. spectra were taken at 25 °C with a JEOL JMN-C-60HL instrument at 60 MHz (Me_4Si as internal standard). I.r. spectra were recorded with a JASCO A-100 spectrometer. Column chromatography was performed with Fuji-Davison silica gel BW-300.

o-Acetylbenzoic acid (**1b**) [12] and *o*-benzoylbenzoic acid (**1c**) [13] were prepared according to the literature method.

N-*Methyl-2-formylbenzamide* (**1d**).—To a solution of *N*-methylphthalimide (1.00 g, 6.21 mmol) in absolute ethanol (50 ml) cooled in ice–water under nitrogen was added $NaBH_4$ (2.60 g, 6.78 mmol). The mixture was stirred at 0—5 °C for 2 h while 3M HCl in ethanol was added (2 drops every 1.5 min). The mixture was poured into water (200 ml) and extracted with methylene dichloride (6 × 50 ml). The combined extracts were washed with saturated aqueous NaCl (2 × 50 ml), dried (Na_2SO_4), and evaporated under reduced pressure to give *N*-methyl-2-formylbenzamide (812 mg, 80%) as a colourless solid; m.p. 129—130 °C (lit.,[14] 131 °C); δ($CDCl_3$) 7.70—7.37 (m, 4 H), 5.57 (d, 1 H, *J* 11.3 Hz), 4.05 (d, 1 H, *J* 11.3 Hz, OH), and 2.90 (s, 3 H); $\nu_{max.}$ (neat) 3 300, 3 050, 2 975, and 1 680 cm^{-1} (Found: C, 66.2; H, 5.6; N, 8.6. Calc. for $C_9H_9NO_2$: C, 66.25; H, 5.6; N, 8.6%).

N-*Methyl-2-acetylbenzamide* (**1e**).—To a stirred solution of *N*-methylphthalimide (500 mg, 3.10 mmol) in dry THF–ether (1:1; 10 ml) under nitrogen was added dropwise a solution of methylmagnesium iodide (0.49M; 13.9 ml, 6.83 mmol) in ether at room temperature. After stirring for 3 h, saturated aqueous NH_4Cl (50 ml) was added, and the mixture was partitioned between water and $CHCl_3$. The aqueous phase was extracted with $CHCl_3$, and the combined organic phase and extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The residue was chromatographed on a silica gel column [elution with ethyl acetate–hexane (1:1)] to provide *N*-methyl-2-acetylbenzamide as a colourless solid (462 mg, 84%), m.p. 128—130.5 °C (lit.,[15] 128—130 °C); δ($CDCl_3$) 7.67—7.24 (m, 4 H), 4.48 (s, 1 H, OH), 2.17 (s, 3 H), and 1.39 (s, 3 H); $\nu_{max.}$($CHCl_3$) 3 320, 3 300, 1 685, 1 600, 1 480, and 1 425 cm^{-1} (Found: C, 67.9; H, 6.3; N, 7.7. Calc. for $C_{10}H_{11}NO_2$: C, 67.8; H, 6.3; N, 7.9%).

N-*Phenyl-2-acetylbenzamide* (**1g**).—This was prepared in the same manner from *N*-phenylphthalimide and methylmagnesium bromide and recrystallized from ethyl acetate (81% yield) to give colourless crystals, m.p. 193—195 °C (lit.,[16] 189—192 °C); δ($CDCl_3$) 7.70—7.31 (m, 9 H), 3.54 (s, 1 H), and 1.62 (s, 3 H); $\nu_{max.}$(THF) 3 320, 1 715, and 1 600 cm^{-1} (Found: C, 75.5; H, 5.6; N, 5.9. $C_{15}H_{13}NO_2$ requires C, 75.3; H, 5.5; N, 5.85%).

N-*Methyl-2-benzoylbenzamide* (**1f**).—This was prepared in 72% yield from *N*-methylphthalimide and phenylmagnesium bromide, as a colourless solid, m.p. 188—189 °C (lit.,[17] 182—182.5 °C); δ($CDCl_3$) 7.65—7.34 (m, 9 H), 4.48 (s, 1 H), and 2.63 (s, 3 H); $\nu_{max.}$(THF) 3 310 and 1 710 cm^{-1} (Found: C, 75.4; H, 5.45; N, 5.8. Calc. for $C_{15}H_{13}NO_2$: C, 75.3; H, 5.5; N, 5.85%).

N-*Phenyl-2-benzoylbenzamide* (**1h**).—This was prepared in 54% yield from *N*-phenylphthalimide and phenylmagnesium bromide as a colourless solid (from ethyl acetate), m.p. 178.5—180 °C (lit.,[18] 192—193 °C from acetic acid); δ($CDCl_3$) 7.85—7.10 (m, 14 H) and 3.84 (s, 1 H); $\nu_{max.}$(THF) 3 270 and 1 715 cm^{-1} (Found: C, 79.8; H, 5.05; N, 4.5. Calc. for $C_{20}H_{15}NO_2$: C, 79.7; H, 5.0; N, 4.65%).

General Procedures for Azide Functionalization.—Method A. To a solution of compound (**1**) (1.00 mmol) in benzene (1.5 ml) was added thionyl chloride (1.50 mmol) at room temperature under nitrogen. The mixture was stirred for 48 h, then evaporated under reduced pressure. To the residue was added benzene (2 ml) to give a solution which was added dropwise to a stirred mixture of saturated aqueous NaN_3 (3.00 mmol) and Aliquat 336 (100 mg) as phase-transfer catalyst. The mixture was stirred for 1 h at room temperature then extracted with ether (5 × 30 ml). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure, and the residue was chromatographed on a silica gel column [elution with ethyl acetate–hexane (1:4)] to provide the azide (**2**), (**3**), or (**9**) [except for entry 5 in Table 1, where methylene dichloride–hexane (1:1) was used for elution].

Method B. To a solution of compound (**1**) (1.00 mmol) in benzene (1.5 ml) was added thionyl chloride (1.50 mmol) at room temperature under nitrogen. The mixture was stirred for 48 h, then evaporated under reduced pressure. To the residue

was added acetonitrile (5 ml) under nitrogen, followed by tetrabutylammonium azide (1.15 mmol). The mixture was stirred for 1 h at room temperature, then evaporated under reduced pressure, and the residue was chromatographed on a silica gel column [elution with ethyl acetate–hexane (1:4 to 1:1)] to provide the azide (**9**) or (**12**).

Method C. To a solution of compound (**1**) (1.00 mmol) in benzene (2 ml) were added diphenylphosphoryl azide (1.00 mmol) and triethylamine (1.10 mmol) at room temperature under nitrogen. The mixture was stirred for several days, then evaporated under reduced pressure and the residue was chromatographed on a silica gel column [elution with ethyl acetate–hexane (1:4 to 1:1)] to provide the azide (**2**)—(**4**), (**6**), or (**7**).

Method D. To a stirred mixture of compound (**1**) (1.00 mmol) and trimethylsilyl azide (1.40 mmol) in methylene dichloride (4 ml) was added dropwise boron trifluoride–ether complex (1.10 mmol) at −78 °C under nitrogen. The resulting solution was stirred at −78 °C until (**1**) was consumed (t.l.c.) and then quenched with saturated aqueous sodium hydrogencarbonate (*ca.* 2 ml). After vigorous stirring for 10 min at room temperature, the mixture was extracted with ether (5 × 30 ml). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure, and the residue was chromatographed on a silica gel column [elution with ethyl acetate–hexane (1:4)] to provide the azide (**7**) or (**10**).

3-*Azidophthalide* (**2**) was obtained in 84% yield by Method A and 92% yield by Method B as a colourless oil, δ(CCl_4) 8.00—7.45 (m, 4 H) and 6.45 (s, 1 H); $\nu_{max.}$(neat) 2 120, 1 780, and 1 600 cm^{-1} (Found: C, 55.0; H, 3.0; N, 23.7. $C_8H_5N_3O_2$ requires C, 54.9; H, 2.9; N, 24.0%).

3-*Azido*-3-*methylphthalide* (**3**) was prepared in 79% yield by Method A and quantitatively by Method C as a colourless solid; δ(CCl_4) 8.00—7.40 (m, 4 H), and 1.86 (s, 3 H); $\nu_{max.}$(CCl_4) 2 100, 1 780, 1 600, and 1 465 cm^{-1} (Found: C, 57.4; H, 3.9; N, 21.9. $C_9H_7N_3O_2$ requires C, 57.1; H, 3.7; N, 22.2%).

3-*Azido*-3-*phenylphthalide* (**4**) was prepared in 91% yield by Method A and 28% yield by Method C as a colourless solid; δ($CDCl_3$) 8.03—7.07 (m, 9 H); $\nu_{max.}$($CHCl_3$) 2 115, 1 798, 1 600, 1 500, 1 470, and 1 450 cm^{-1} (Found: C, 66.9; H, 3.8; N, 16.6. $C_{14}H_9N_3O_2$ requires C, 66.9; H, 3.6; N, 16.7%).

o-Benzoylbenzoic acid azide (**5**) was not isolated, but was characterized by the i.r. spectrum of a mixture of (**4**) and (**5**): $\nu_{max.}$(neat) 2 150, 1 700, and 1 680 cm^{-1}.

3-*Azido*-2,3-*dihydro*-2-*methylisoindol*-1-*one* (**6**) was prepared in 74% yield as a colourless solid; δ($CDCl_3$) 8.00—7.50 (m, 4 H), 5.40 (s, 1 H), and 3.18 (s, 3 H); $\nu_{max.}$($CHCl_3$) 2 100 and 1 700 cm^{-1} (Found: C, 57.4; H, 4.2; N, 29.7. $C_9H_8N_4O$ requires C, 57.4; H, 4.3; N, 29.8%).

3-Azido-2,3-dihydro-2,3-dimethylisoindol-1-one (**7**) was prepared in 18% yield as a colourless solid and 2,3-*dihydro*-2-*methyl*-3-*methyleneisoindol*-1-*one* (**8**) was obtained in 36% yield as a colourless solid by Method C. By Method D, (**7**) and (**8**) were prepared in 70% and 11% yields, respectively. The product (**7**) showed δ($CDCl_3$) 7.95—7.50 (m, 4 H), 3.09 (s, 3 H), and 1.66 (s, 3 H); $\nu_{max.}$($CHCl_3$) 3 000, 2 120, 1 705, and 1 600 cm^{-1}; *m/z* 202 (M^+). Compound (**8**) had m.p. 97—100 °C; δ($CDCl_3$) 8.00—7.40 (m, 4 H), 5.19 (d, 1 H, *J* 2.0 Hz), 4.82 (d, 1 H, *J* 2.0 Hz), and 3.26 (s, 3 H); $\nu_{max.}$($CHCl_3$) 1 700, 1 640, 1 470, and 1 430 cm^{-1} (Found: C, 75.3; H, 5.9; N, 8.74. $C_{10}H_9NO$ requires C, 75.45; H, 5.7; N, 8.8%).

3-*Azido*-2,3-*dihydro*-2-*methyl*-3-*phenylisoindol*-1-*one* (**9**) was prepared in 30% yield as a colourless solid by Method A and in 75% yield by Method B [by Method C, (**9**) was not obtained]; δ($CDCl_3$) 8.00—7.20 (m, 4 H), 7.70 (s, 5 H), and 2.90 (s, 3 H); $\nu_{max.}$($CHCl_3$) 3 070, 2 100, 1 700, 1 600, 1 475, 1 455, and 1 415 cm^{-1} (Found: C, 68.1; H, 4.6; N, 21.2. $C_{15}H_{12}N_4O$ requires C, 68.2; H, 4.6; N, 21.2%).

3-*Azido*-2,3-*dihydro*-3-*methyl*-2-*phenylisoindol*-1-*one* (**10**) and 2,3-*dihydro*-3-*methylene*-2-*phenylisoindol*-1-*one* (**11**) were obtained in 33% and 52% yields, respectively, as colourless solids by Method D. Compound (**10**) showed δ($CDCl_3$) 8.05—7.30 (m, 9 H) and 1.65 (s, 3 H); $\nu_{max.}$($CHCl_3$) 3 010, 2 110, 1 715, 1 600, 1 500, and 1 475 cm^{-1} (Found: C, 68.0; H, 4.7; N, 21.2. $C_{15}H_{12}N_4O$ requires C, 68.2; H, 4.6; N, 21.2%). Compound (**11**) had m.p. 85 °C (decomp.); δ($CDCl_3$) 8.05—7.28 (m, 9 H), 5.23 (d, 1 H, *J* 1.95 Hz), and 4.80 (d, 1 H, *J* 1.95 Hz); $\nu_{max.}$($CHCl_3$) 3 010, 1 715, 1 650, 1 600, and 1 505 cm^{-1} (Found: C, 81.3; H, 5.2; N, 6.25. $C_{15}H_{11}NO$ requires C, 81.4; H, 5.0; N, 6.3%).

3-*Azido*-2,3-*dihydro*-2,3-*diphenylisoindol*-1-*one* (**12**) was prepared in 99% yield as a colourless solid by Method B; δ($CDCl_3$) 8.10—7.40 (m, 4 H) and 7.27 (s, 10 H); $\nu_{max.}$($CHCl_3$) 3 060, 2 110, 1 720, 1 600, 1 500, 1 470, and 1 450 cm^{-1} (Found: C, 73.8; H, 4.5; N, 16.9. $C_{20}H_{14}N_4O$ requires C, 73.6; H, 4.3; N, 17.2%).

3-Azido-3-methylfuro[3,4-*b*]pyridin-1(3*H*)-one (**14**) was prepared in 94% yield as a colourless solid by Method C; δ($CDCl_3$) 8.95 (dd, 1 H, *J* 1.5 and 4.9 Hz), 8.24 (dd, 1 H, *J* 1.5 and 7.8 Hz), 7.59 (dd, 1 H, *J* 4.9 and 7.8 Hz), and 1.99 (s, 3 H); $\nu_{max.}$($CHCl_3$) 3 000, 2 120, 1 785, 1 600, 1 475, and 1 430 cm^{-1}; *m/z* 148 ($M^+ - N_3$).

3-*Azido*-3-*methylfuro*[3,4-b]*pyridin*-1(3H)-*one* 4-*oxide* (**16**) was prepared in 99% yield as a colourless solid by Method C; δ($CDCl_3$) 8.48 (dd, 1 H, *J* 1.5 and 5.7 Hz), 7.85—7.36 (m, 2 H), and 2.21 (s, 3 H); $\nu_{max.}$($CHCl_3$) 3 100, 3 000, 2 120, 1 795, 1 620, 1 580, and 1 440 cm^{-1} (Found: C, 46.6; H, 3.1; N, 26.9. $C_8H_6N_4O_3$ requires C, 46.6; H 2.9; N, 27.2%).

General Procedure for the Thermal Decomposition of Azides.—The azide (1.00 mmol) was heated to reflux in xylene (b.p. 138.5—141.5 °C; 4 ml) under nitrogen for several hours (t.l.c.-monitored). The mixture was evaporated under reduced pressure and the residue which was chromatographed on a silica gel column [elution with ethyl acetate–hexane (1:4)] to provide rearrangement products as analytically pure solids (Table 2).

3-*Iminophthalide* (**18a**) was a colourless solid, m.p. 112—116 °C; δ[$(CD_3)_2SO$] 11.32 (br s, 1 H) and 7.83 (s, 4 H); $\nu_{max.}$(KBr) 3 200—2 700, 2 300, 1 770, and 1 730—1 660 cm^{-1} (Found: C, 65.25; H, 3.45; N, 9.55. $C_8H_5NO_2$ requires C, 65.3; H, 3.4; N, 9.5%), which seems to exist largely in the chain form (*o*-cyanobenzoic acid).

2-*Methyl*-3,1-*benzoxazin*-4-*one* (**17b**) was a colourless solid, m.p. 80—82 °C; δ($CDCl_3$) 8.20—7.34 (m, 4 H) and 2.47 (s, 3 H); $\nu_{max.}$(CH_2Cl_2) 1 760, 1 655, and 1 610 cm^{-1} (Found: C, 67.1; H, 4.5; N, 8.6. $C_9H_7NO_2$ requires C, 67.1; H, 4.4; N, 8.7%).

2-*Phenyl*-3,1-*benzoxazin*-4-*one* (**17c**) was a colourless solid, m.p. 122—124 °C; δ($CDCl_3$) 8.41—8.17 (m, 3 H) and 7.87—7.41 (m, 6 H); $\nu_{max.}$(CCl_4) 1 770, 1 630, 1 620, 1 600, 1 580, and 1 480 cm^{-1} (Found: C, 75.2; H, 4.2; N, 6.1. $C_{14}H_9NO_2$ requires C, 75.3; H, 4.1; N, 6.3%).

3-(*Phenylimino*)*phthalide* (**18c**) was a yellow solid, m.p. 122—123 °C; δ($CDCl_3$) 8.19—7.69 (m, 4 H) and 7.48—7.25 (m, 5 H); $\nu_{max.}$(CCl_4) 1 805 and 1 700 cm^{-1} (Found: C, 75.2; H, 4.2; N, 6.1. $C_{14}H_9NO_2$ requires C, 75.3; H, 4.1; N, 6.3%).

2,3-*Dihydro*-3-*imino*-2-*methylisoindol*-1-*one* (**18d**) was a pale yellow solid, m.p. 138—141 °C; δ($CDCl_3$) 8.00—7.50 (m, 5 H, aromatic and NH) and 3.31 (s, 3 H); $\nu_{max.}$($CHCl_3$) 3 320, 1 740, 1 660, and 1 450 cm^{-1} (Found: C, 67.65; H, 5.0; N, 17.3. $C_9H_8N_2O$ requires C, 67.5; H, 5.0; N, 17.5%).

3-*Methyl*-2-*phenylquinazolin*-4(3H)-*one* (**17e**) was a colourless solid, m.p. 134—135.5 °C; δ($CDCl_3$) 8.34 (ddd, 1 H, *J* 1.0, 1.5, and 7.3 Hz), 7.83—7.35 (m, 3 H), 7.54 (s, 5 H), and 3.50 (s, 3 H); $\nu_{max.}$($CHCl_3$) 1 670, 1 610, 1 600, and 1 570 cm^{-1} (Found: C, 76.4; H, 5.15; N, 11.7. $C_{15}H_{12}N_2O$ requires C, 76.25; H, 5.1; N, 11.9%).

2,3-*Dihydro*-2-*methyl*-3-*phenyliminoisoindol*-1-*one* (**18e**) was a pale yellow solid, m.p. 140.5—143 °C; δ($CDCl_3$) 7.94—6.89

(m, 9 H) and 3.36 (s, 3 H); $\nu_{max.}$($CHCl_3$) 1 730, 1 670, 1 600, 1 470, and 1 430 cm^{-1} (Found: C, 75.9; H, 5.2; N, 12.1. $C_{15}H_{12}N_2O$ requires C, 76.25; H, 5.1; N, 11.9%).

2,3-*Diphenylquinazolin*-4(3H)-*one* (**17f**) was a colourless solid, m.p. 156.5—157.5 °C; δ($CDCl_3$) 8.37 (ddd, 1 H, *J* 1.0, 1.5, and 7.3 Hz) and 7.87—7.07 (m, 13 H); $\nu_{max.}$($CHCl_3$) 3 060, 1 685, 1 600, 1 585, and 1 560 cm^{-1} (Found: C, 80.4; H, 5.0; N, 9.3. $C_{20}H_{14}N_2O$ requires C, 80.5; H, 4.7; N, 9.4%).

2,3-*Dihydro*-2-*phenyl*-3-*phenyliminoisoindol*-1-*one* (**18f**) was separated from (**17f**), but could not be separated from (**12**) which had not disappeared after heating for 14 h. Although the mixture of (**18f**) and (**12**) was chromatographed on a silica gel column (eluted with methylene dichloride), the separation was not successful. The solution of (**18f**) and (**12**) in methylene dichloride was evaporated under reduced pressure (0.5 mmHg; room temperature; 12 h) to give a viscous oil, which contained (**18**), (**12**), and methylene dichloride (i.r. and mass spectra). The ratios of (**18f**), (**12**), and methylene dichloride were determined by elemental analysis. The mixture showed $\nu_{max.}$(neat) 3 060, 2 110 [N_3 of (**12**)], 1 740 [C=N of (**18f**)], 1 720 [C=O of (**12**)], 1 670 [C=O of (**18f**)], 1 600, 1 500, 1 470, 1 450, 760 (CH_2Cl_2), 715, and 700 cm^{-1}; *m/z* 326, 298 (M^+) and 284 [Found: C, 73.5; H, 4.6; N, 11.0. Calc. for (**17f**):(**12**):CH_2Cl_2 = 1.00:0.425:0.400: C, 73.7; H, 4.4; N, 11.0%].

8-*Methylpyrido*[2,3-d][1,2]*oxazin*-5-*one* (**19g**) was a colourless solid, m.p. 120.5—122.5 °C; δ($CDCl_3$) 8.97 (dd, 1 H, *J* 1.7 and 4.9 Hz), 8.18 (dd, 1 H, *J* 1.7 and 7.6 Hz), 7.61 (dd, 1 H, *J* 4.9 and 7.6 Hz), and 3.26 (s, 3 H); $\nu_{max.}$($CHCl_3$) 3 010, 1 725, 1 600, 1 440, and 1 415 cm^{-1} (Found: C, 59.5; H, 3.9; N, 17.0. $C_8H_6N_2O_2$ requires C, 59.3; H, 3.7; N, 17.3%).

8-*Methylpyrido*[2,3-d][1,2]*oxazin*-5-*one* 1-*oxide* (**19h**) was a colourless solid, m.p. 248—250 °C (decomp.); δ($CDCl_3$) 8.37 (dd, 1 H, *J* 2.1 and 5.5 Hz), 7.73—7.36 (m, 2 H), and 3.22 (s, 3 H); $\nu_{max.}$($CHCl_3$) 1 730, 1 600, 1 440, and 1 415 cm^{-1} (Found: C, 54.05; H, 3.6; N, 15.4. $C_8H_6N_2O_3$ requires C, 53.9; H, 3.4; N, 15.7%).

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