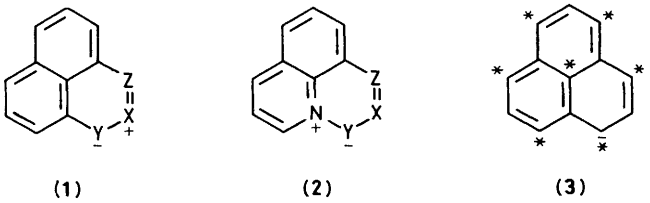
Heterocyclic Mesomeric Betaines. Part 2.[1] Synthesis of a Hetero Derivative of the Benzo[*b*]phenalenide Anion

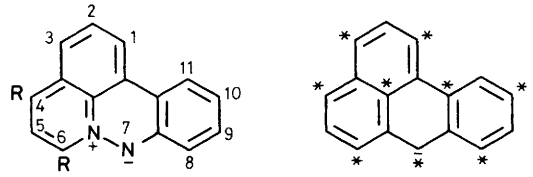
W. David Ollis * **and Stephen P. Stanforth**
Department of Chemistry, The University, Sheffield S3 7HF
Christopher A. Ramsden
The Research Laboratories, May and Baker Ltd., Dagenham, Essex RM10 7XS

Reductive cyclization of 2,4-dimethyl-8-(2-nitrophenyl)quinoline with hot triethyl phosphite afforded 2,4-dimethyl-7*H*-pyrido[3,2-*c*]carbazole (**10**) and 4,6-dimethyl-6aλ^5,7-diazabenz[*de*]anthracen-6a-ium-7-ide (**4**; R = Me). The latter is the first example of a conjugated heterocyclic mesomeric betaine isoconjugate with the benzo[*b*]phenalenide anion.

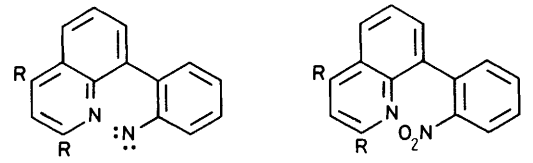
Representatives of two types [(**1**) and (**2**)] of conjugated heterocyclic mesomeric betaines have been synthesized which are isoconjugate with the tricyclic odd alternant phenalenide anion (**3**). The first type includes the compounds (**1**; X = NR, Y = Z = CR),[2,3] (**1**; X = S, Y = Z = CR),[4–6] (**1**; X = NR, Y = Z = N),[7–20] (**1**; X = S, Y = Z = N),[21–24] and (**1**; X = Se, Y = Z = N).[25,26] The second type includes the compounds (**2**; X = CR, Y = Z = N),[27–29] and (**2**; X = CR, Y = CH, Z = N).[1,30,31] We now report upon the synthesis and cycloaddition reaction with dimethyl acetylenedicarboxylate of the conjugated heterocyclic mesomeric betaine (**4**; R = Me) which is a benzo derivative of the second type. This is the first example of a heterocyclic mesomeric betaine[32] which is isoconjugate with the tetracyclic odd alternant benzo[*b*]-phenalenide anion (**5**).



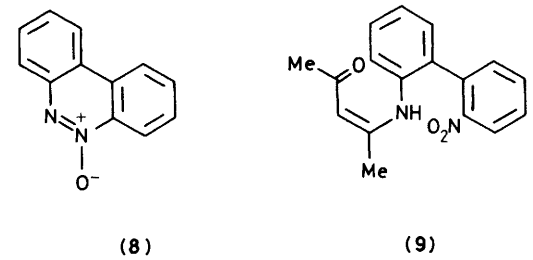
(1) (2) (3)



(4) (5)



(6) (7)



(8) (9)

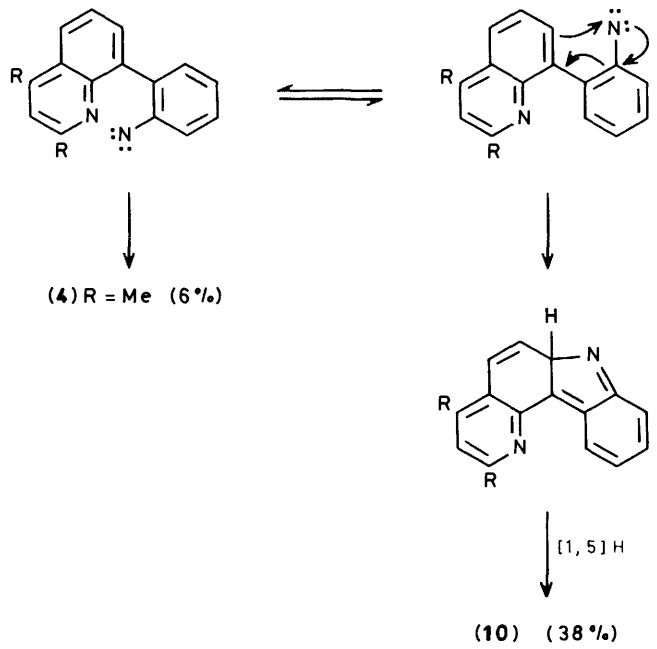
Our synthetic approach was based upon the well-established methodology for the formation of azomethine imides by nitrogen lone pair insertion by nitrenes.[33,34] The nitrene (**6**) or its equivalent was to be generated by deoxygenation of the corresponding 8-(2-nitrophenyl)quinoline (**7**; R = H) by heating with triethyl phosphite.

Application of the Skraup reaction to 2-amino-2′-nitrobiphenyl was disappointing in that the yield of the quinoline (**7**; R = H) was low (5%): benzo[*c*]cinnoline *N*-oxide (**8**)[35] was formed (5% yield). Attention was therefore directed towards the synthesis of the dimethyl derivative (**4**; R = Me). The required 2,4-dimethyl-8-(2-nitrophenyl)quinoline (**7**; R = Me) was obtained (67% yield) by the acid-catalysed cyclodehydration of the condensation product (**9**) of 2-amino-2′-nitrobiphenyl with acetylacetone.

Deoxygenation of 2,4-dimethyl-8-(2-nitrophenyl)quinoline (**7**; R = Me) with hot triethyl phosphite gave two products. The major product was shown to be the carbazole (**10**) (38% yield) and the minor product was the required conjugated heterocyclic mesomeric betaine (**4**) (6% yield). The two pathways for the transformation of the nitrene (**6**) or its equivalent into the products (**4**) and (**10**) are formally represented in the Scheme. This Scheme portrays the competition between the two pathways (**6**) ⟶ (**4**) and (**6**) ⟶ (**10**). These electrophilic reactions presumably involve nitrenes (singlet or triplet) or their equivalent or nitrogen-phosphorus covalent intermediates. Experimental evidence is not available to distinguish between these possibilities.

4,6-Dimethyl-6aλ^5,7-diazabenz[*de*]anthracen-6a-ium-7-ide (**4**; R = Me) is a red, air-sensitive solid, m.p. 150—153 °C. Its structure was established from its spectroscopic properties. High resolution mass spectrometry established the molecular formula, $C_{17}H_{15}N_2$. Its ^{1}H n.m.r. spectrum showed eight aromatic protons (δ 7.4—6.7)[14] and two methyl groups (δ 2.10 and 2.29). The conjugated heterocyclic mesomeric betaine (**4**; R = Me) with perchloric acid in acetic acid gave the yellow perchlorate (**11**).

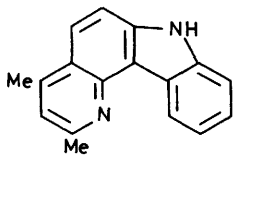
1,3-Dipolar cycloaddition was observed when the conjugated mesomeric betaine (**4**; R = Me) was treated with dimethyl acetylenedicarboxylate in boiling toluene. The constitution (**12**) of the cycloadduct was firmly established from its spectroscopic properties. High resolution mass spectrometry established the molecular formula, $C_{23}H_{20}N_2O_4$. Its ^{1}H n.m.r. spectrum

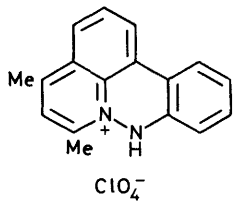


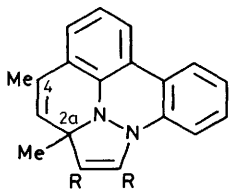
Scheme.

showed seven aromatic protons (δ 7.61—6.95), two methoxycarbonyl groups (δ 3.81 and δ 3.69), one quaternary methyl group (δ 1.54), and the MeC=CH system [(δ 2.04, d, *J* 1.5 Hz, Me) and (δ 6.00, q, *J* 1.5 Hz, C=CH)]. The formation of the cycloadduct (**12**) is in accord with expectation and provides supporting evidence for the constitution of the conjugated heterocyclic mesomeric betaine (**4**; R = Me).

The formation of the two products, (**4**) and (**10**), in the triethyl phosphite promoted reductive cyclization of the 2-nitrophenyl compound (**7**; R = Me) contrasts with corresponding earlier results (Figure). In connection with possible mechanisms for these two reactions, it was established that the heterocyclic mesomeric betaine (**4**) is not thermally transformed into the covalent isomer (**10**) under the reaction conditions which are associated with their formation. Thus the two reactions, (**7**) ⟶ (**4**) and (**7**) ⟶ (**10**), involve two competing processes (Scheme) which are irreversible. The analogous five reactions[34g,36–41] (Figure), leading in each case to only one product, have been regarded as cyclizations involving electrophilic nitrene intermediates which participate either in N–N bond formation (two reactions) or in C–N bond formation (three reactions). The C–N bond formation products could just be regarded as C–H bond insertion products from the nitrene. However, an appealing mechanistic alternative is that the three C–N bond formation products which are observed (Figure) and the transformation (**7**) ⟶ (**4**) now reported, all involve 6π-electrocyclization giving an intermediate which then undergoes a 1,5-sigmatropic hydrogen shift (Figure).


(10)


(11)


(12) R = CO_2Me

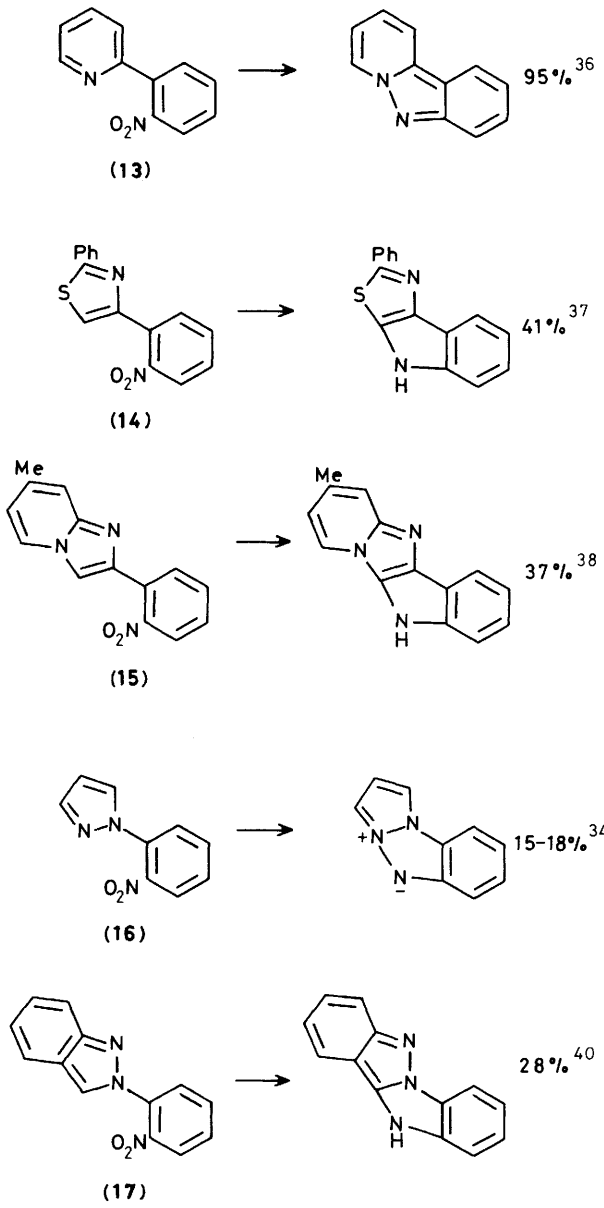


Figure.

Experimental

General experimental directions are given in Part 1.[1]

8-(2′-*Nitrophenyl*)*quinoline* (**7**; R = H).—A mixture of arsenic pentaoxide (2.0 g), boric acid (1.0 g), and glycerol (4.0 g) was stirred at 90 °C and concentrated sulphuric acid (2.4 ml) was added dropwise (5 min). 2-Amino-2′-nitrobiphenyl (2.5 g) was then added in portions over a period of 50 min and the mixture was then heated at 130 °C (5.5 h). Water (20 ml)

followed by ammonia solution (*d* 0.88; 10 ml) were then added to the cooled mixture and the resulting dark solid was collected and extracted with hot ethanol (3 × 50 ml). The combined ethanolic extracts were evaporated and the residue was fractionated by preparative thick layer chromatography (silica gel; ether–light petroleum, 1:1). The first component (R_F 0.46) gave 8-(*2′-nitrophenyl*)*quinoline* (**7**; R = H) (150 mg, 5%) as colourless prisms, m.p. 152—154 °C (from ethanol) (Found: C, 72.2; H, 4.2; N, 11.3%; $M^{+\cdot}$, 250. $C_{15}H_{10}N_2O_2$ requires C, 72.0; H, 4.0; N, 11.2%; *M*, 250); $\nu_{max.}$ 1 525 and 1 355 cm^{-1}; δ 8.79 (1 H, dd, $J_{2,3}$ 4 Hz and $J_{2,4}$ 1.5 Hz, 2-H), 8.17 (1 H, dd, $J_{3,4}$ 9 Hz and $J_{2,4}$ 1.5 Hz, 4-H), 8.10 (1 H, dd, $J_{3'4'}$ 8 Hz and $J_{3'5'}$ 1.5 Hz, 3′-H), 7.87 (1 H, dd, *J* 8 and 1.5 Hz), 7.5—7.8 (5 H, m), and 7.37 (1 H, dd, $J_{3,4}$ 9 Hz and $J_{2,3}$ 4 Hz, 3-H).

The second component (R_F 0.24) gave benzo[*c*]cinnoline *N*-oxide (**8**) (100 mg, 5%) as cream needles, m.p. 138—140 °C (from di-isopropyl ether) (lit.,[35] 139—141 °C).

2-(*2′-Nitrobiphenyl-2-ylamino*)*pent-2-en-4-one* (**9**).—2-Amino-2′-nitrobiphenyl[42] (13.1 g), acetylacetone (9 ml), and calcium sulphate (18.0 g) were heated on a steam-bath (16 h). The cooled mixture was extracted with boiling ether (2 × 50 ml) and the combined ethereal extracts were concentrated to give a yellow solid. Recrystallization from ethanol gave the *title compound* (**9**) (6.5 g, 36%) as large yellow rhombs, m.p. 105—106 °C [Found: C, 68.7; H, 5.6; N, 9.4%; *m/z* 297 (*M* + 1). $C_{17}H_{16}N_2O_3$ requires C, 68.9; H, 5.5; N, 9.5%; *M*, 296]; $\nu_{max.}$ 2 290, 1 610, 1 570, 1 520, 1 355, and 1 275 cm^{-1}; δ 12.11 (1 H, br s, NH), 7.98 (1 H, dd, *J* 8 and 1.5 Hz), 7.68 (1 H, dt, *J* 8 and 1.5 Hz), 7.50 (1 H, dt, *J* 7 and 1.5 Hz), 7.4—7.2 (4 H, m), 7.16 (1 H, d, *J* 8 Hz), 5.10 (1 H, s, 3-H), and 1.92 (6 H, s, 2 × CH_3); δ_C 196.0 (C-4), 159.9, 148.6, 136.6, 133.9, 133.3, 133.0, 132.3, 129.3, 129.0, 128.6, 125.9, 124.4, 98.1, 28.9 (CH_3), and 19.2 (CH_3).

2,4-*Dimethyl*-8-(*2′-nitrophenyl*)*quinoline* (**7**; R = Me).—A solution of compound (**9**) (8.9 g) in concentrated sulphuric acid (20 ml) was heated on a steam-bath (16 h). The cooled solution was made alkaline by addition of aqueous sodium carbonate and extracted with dichloromethane (4 × 50 ml). The combined organic fractions were washed with water (3 × 50 ml), dried ($MgSO_4$), and evaporated to give a solid residue. Recrystallization from ethanol gave the *title compound* (**7**; R = Me) (5.6 g, 67%) as colourless plates, m.p. 143—145 °C [Found: C, 73.6; H, 4.8; N, 10.2%; *m/z* 232 (*M* − NO_2). $C_{17}H_{14}N_2O_2$ requires C, 73.4; H, 5.1; N, 10.1%; *M*, 278]; $\nu_{max.}$ 1 610, 1 525, and 1 360 cm^{-1}; δ 8.00 (2 H, m), 7.4—7.8 (5 H, m), 7.06 (1 H, s, 3-H), 2.60 (3 H, s, CH_3), and 2.48 (3 H, s, CH_3).

Reaction of 2,4-*Dimethyl*-8-(*2′-nitrophenyl*)*quinoline* (**7**; R = Me) *with Triethyl Phosphite*.—A mixture of compound (**7**; R = Me) (0.5 g) and triethyl phosphite (5.0 ml) was heated at 120 °C under a nitrogen atmosphere (3 days). Chloroform (5 ml) was then added to the cooled reaction mixture and the resulting fawn solid was collected. Recrystallization of this from methanol gave 2,4-*dimethyl*-7H-*pyrido*[3,2-c]*carbazole* (**10**) (167 mg, 38%) as tan rhombs, m.p. 251 °C (Found: $M^{+\cdot}$, 246.1140. $C_{17}H_{14}N_2$ requires *M*, 246.1157); $\nu_{max.}$ 3 485, 1 600, and 1 320 cm^{-1}; δ([$^2H_5$]pyridine) 12.78 (1 H, s, NH), 9.67 (1 H, m) (AB system, δ_A 7.93, δ_B 7.81, J_{AB} 9 Hz, 5-H and 6-H), 7.75 (1 H, m), 7.55 (2 H, m), 7.00 (1 H, s, 3-H), 2.80 (3 H, s, CH_3), and 2.54 (3 H, s, CH_3).

The chloroform-soluble portion of the reaction mixture was evaporated and the residue was fractionated by preparative thick layer chromatography (silica gel; ether–light petroleum, 1:1). The orange band was collected and yielded a red semisolid (77 mg). Trituration of this with acetonitrile afforded 4,6-*dimethyl*-6aλ^5,7-*diazabenz*[de]*anthracen*-6a-*ium*-7-*ide* (**4**; R = Me) (28 mg, 6%) as a red solid, m.p. 150—153 °C (Found: $M^{+\cdot}$, 246.1169. $C_{17}H_{14}N_2$ requires *M*, 246.1157); δ 7.39 (1 H, dd, *J* 8 and 2 Hz), 7.15—7.20 (3 H, m), 6.80—6.92 (2 H, m), 6.67 (2 H, m), 2.29 (3 H, s, CH_3), and 2.10 (3 H, s, CH_3).

Thermal Stability of 4,6-*Dimethyl*-6aλ^5,7-*diazabenz*[de]*anthracen*-6a-*ium*-7-*ide* (**4**; R = Me).—This compound was recovered unchanged when heated (120 °C; 40 h) in triethyl phosphite under a nitrogen atmosphere.

4,6-*Dimethyl*-6aλ^5,7-*diazabenz*[de]*anthracen*-6a-*ium Perchlorate* (**11**).—Perchloric acid (60%; 5 drops) was added to a solution of compound (**4**; R = Me) (40 mg) in glacial acetic acid (0.5 ml). Dilution of the mixture with ether precipitated 4,6-*dimethyl*-6aλ^5,7-*diazabenz*[de]*anthracen*-6a-*ium perchlorate* (**11**) (26 mg, 46%), as a yellow solid, m.p. > 300 °C. An analytically pure sample was obtained by dissolution in hot acetonitrile and reprecipitation with ether (Found: C, 58.5; H, 4.2; N, 7.8; Cl, 10.2. $C_{17}H_{15}N_2ClO_4$ requires C, 58.9; H, 4.4; N, 8.1; Cl, 10.2%); $\nu_{max.}$(KBr) 3 650—2 800br, 1 610, 1 585, 1 145, 1 115, 1 085, and 770 cm^{-1}.

Reaction of the Conjugated Heterocyclic Mesomeric Betaine (**4**; R = Me) *with Dimethyl Acetylenedicarboxylate*.—A solution of compound (**4**; R = Me) (16 mg) and dimethyl acetylenedicarboxylate (0.05 ml) in boiling dry toluene (1.0 ml) was heated (2 h) under a nitrogen atmosphere. The reaction mixture was evaporated and fractionated by preparative thick layer chromatography (silica gel; ether). The fraction (R_F 0.86) was collected and recrystallized from acetonitrile to give *dimethyl* 2a,4-*dimethyl*-2aH-11a,11b-*diazabenz*[fg]*aceanthrylene*-1,2-*dicarboxylate* (**12**) (8 mg, 32%) as yellow plates, m.p. 214—217 °C (Found: $M^{+\cdot}$, 388.1420. $C_{23}H_{20}N_2O_4$ requires *M*, 388.1423); $\nu_{max.}$(KBr) 1 750, 1 690, and 1 345 cm^{-1}; δ 7.61 (1 H, m), 7.41 (1 H, dd, *J* 8 and 1.5 Hz), 7.16—7.24 (2 H, m), 7.10 (1 H, dd, *J* 8 and 1.5 Hz), 7.01 (1 H, m), 6.95 (1 H, t, *J* 8 Hz), 6.00 (1 H, q, *J* 1.5 Hz), 3.81 (3 H, s, OCH_3), 3.69 (3 H, s, OCH_3), 2.04 (3 H, d, *J* 1.5 Hz, 4-CH_3), and 1.54 (3 H, s, 2a-CH_3).

Acknowledgements

We warmly thank the S.E.R.C. and May and Baker Ltd. for the award of a CASE Research Studentship (to S. P. S.).

References

1 Part 1, W. D. Ollis, C. A. Ramsden, and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1989, preceding paper.
2 M. Ikeda, Y. Miki, S. Kaita, Y. Nishikawa, and Y. Tamura, *J. Chem. Soc., Perkin Trans. 1*, 1977, 44; M. Ikeda, Y. Goto, T. Niiya, and K. Sumoto, *Heterocycles*, 1984, **22**, 981.
3 A. C. Oehlschlager, A. S. Yim, and M. H. Akhtar, *Can. J. Chem.*, 1978, **56**, 273.
4 M. P. Cava, N. M. Pollack, and D. A. Repella, *J. Am. Chem. Soc.*, 1967, **89**, 3640.
5 R. H. Schlessinger and I. S. Ponticello, *J. Am. Chem. Soc.*, 1967, **89**, 3641.
6 R. H. Schlessinger and A. G. Schultz, *J. Am. Chem. Soc.*, 1968, **90**, 1676.
7 F. Sachs, *Liebigs Ann. Chem.*, 1909, **365**, 53.
8 M. J. Perkins, *J. Chem. Soc.*, 1964, 3005.
9 H. Sieper, *Tetrahedron Lett.*, 1967, 1987.
10 P. Tavs, H. Sieper, and H. Beecken, *Liebigs Ann. Chem.*, 1967, **704**, 150.
11 H. Sieper and P. Tavs, *Liebigs Ann. Chem.*, 1967, **704**, 161.
12 H. Beecken, P. Tavs, and H. Sieper, *Liebigs Ann. Chem.*, 1967, **704**, 166.
13 H. Beecken and P. Tavs, *Liebigs Ann. Chem.*, 1967, **704**, 172.
14 H. Beecken, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 360.
15 A. R. J. Arthur, P. Flowerday, and M. J. Perkins, *J. Chem. Soc., Chem. Commun.*, 1967, 410.

16 C. W. Rees and R. C. Storr, *J. Chem. Soc. C*, 1969, 756.
17 P. Flowerday, M. J. Perkins, and A. R. J. Arthur, *J. Chem. Soc. C*, 1970, 290.
18 C. W. Rees, R. W. Stephenson, and R. C. Storr, *J. Chem. Soc., Chem. Commun.*, 1972, 1281.
19 S. F. Gait, M. J. Rance, C. W. Rees, R. W. Stephenson, and R. C. Storr, *J. Chem. Soc., Perkin Trans. 1*, 1975, 556.
20 P. Spagnolo, A. Tundo, and P. Zanirato, *J. Org. Chem.*, 1978, **43**, 2508.
21 R. Dietz, *J. Chem. Soc., Chem. Commun.*, 1965, 57.
22 H. Behringer and K. Leiritz, *Chem. Ber.*, 1965, **98**, 3196.
23 H. Beecken, *Chem. Ber.*, 1967, **100**, 2164, 2170.
24 I. Yavari, R. E. Botto, and J. D. Roberts, *J. Org. Chem.*, 1978, **43**, 2542.
25 F. Sachs, *Liebigs Ann. Chem.*, 1909, **365**, 135.
26 M. L. Kaplan, R. C. Haddon, F. C. Schilling, J. H. Marshall, and F. B. Bramwell, *J. Am. Chem. Soc.*, 1979, **101**, 3306.
27 Y. Tamura, Y. Miki, H. Hayushi, Y. Sumida, and M. Ikeda, *Heterocycles*, 1977, **6**, 281.
28 M. Ikeda, M. Yamagishi, S. M. M. Bayomi, Y. Miki, Y. Sumida, and Y. Tamura, *J. Chem. Soc., Perkin Trans. 1*, 1983, 349.
29 Y. Tamura, M. Yamagishi, M. Ikeda, and Y. Miki, *Heterocycles*, 1983, **20**, 159.
30 S. Kanemasa, S. Kobira, and S. Kajigaeshi, *Chem. Lett.*, 1980, 951; *Heterocycles*, 1980, **14**, 1107; 1981, **16**, 165.
31 G. Mitchell and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 403.
32 W. D. Ollis, S. P. Stanforth, and C. A. Ramsden, *Tetrahedron*, 1985, **41**, 2239.
33 J. I. G. Cadogan, *Q. Rev., Chem. Soc.*, 1968, **22**, 222; *Synthesis*, 1969, **1**, 11; *Acc. Chem. Res.*, 1972, **5**, 303; C. A. Ramsden, *Tetrahedron*, 1977, **33**, 3203; 'Comprehensive Heterocyclic Chemistry,' ed. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, **6**, 1027; R. K. Smalley and H. Suschitzky, *Chem. Ind. (London)*, 1970, 1338; B. Iddon, O. Meth-Cohn, E. F. V. Scriven, H. Suschitzky, and P. T. Gallagher, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 900; 'Organophosphorus Reagents in Organic Synthesis,' ed. J. I. G. Cadogan, Academic Press, London, 1979; S. R. Challand, *Aromat. Heteroaromat. Chem.*, 1977, **5**, 354; R. S. Atkinson, *ibid.*, 1978, **6**, 234; 1979, **7**, 314; O. Meth-Cohn, *Heterocycles*, 1980, **14**, 1497.
34 (*a*) I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Lett.*, 1976, 925 and 929; (*b*) J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *ibid.*, 1976, 4513; (*c*) I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Res. (S)*, 1977, 17; (*d*) J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2194; (*e*) J. M. Lindley, O. Meth-Cohn, and H. Suschitzky, *ibid.*, 1978, 1198; (*f*) D. G. Hawkins, O. Meth-Cohn, and H. Suschitzky, *ibid.*, 1979, 3207; (*g*) J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *ibid.*, 1980, 982.
35 R. E. Moore and A. Furst, *J. Org. Chem.*, 1958, **23**, 1504.
36 J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.
37 K. T. Potts and J. L. Marshall, *J. Org. Chem.*, 1976, **41**, 129.
38 Part 4, W. D. Ollis, C. A. Ramsden, and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1989, 961.
39 B. M. Lynch and Y. Y. Hung, *J. Heterocycl. Chem.*, 1965, **2**, 218.
40 O. Tsuge and H. Samura, *Org. Prep. Proceed. Int.*, **6**, 161 (*Chem. Abstr.*, 1975, **82**, 4215q).
41 S. P. Stanforth, *J. Heterocycl. Chem.*, 1987, **24**, 531.
42 A. E. S. Fairfull, *J. Chem. Soc.*, 1952, 4700.

Received 24*th February* 1988; *Paper* 8/00731D