Photochemistry of *N*-Acyl-2-nitrodiphenylamines. A Novel Photochemical Synthesis of Phenazine *N*-Oxides [1]

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In contrast with 2-nitrodiphenylamines and their *N*-alkyl derivatives, *N*-acetyl- and *N*-benzoyl-2-nitrodiphenylamines are converted into phenazine *N*-oxides by u.v. irradiation. The requirement of *N*-acyl groupings is best explained in terms of oxygen transfer from the nitro-group to the amide carbonyl group. The reaction has been applied to the synthesis of some condensed pyrazine *N*-oxides (imidazo- and thieno-quinoxaline *N*-oxides).

THE formation of *N*-heterocycles *via* photochemical interaction between an aromatic nitro-group and an ethylenic or acetylenic bond is well established.[2] We report here that irradiation of *N*-acyl-2-nitrodiphenylamines gives phenazine 5-oxides.[1] The observation provides a new preparative method for phenazine *N*-oxides which demonstrates a novel type of photocyclisation involving an aromatic nitro-group and an aromatic C=C bond under the influence of an *N*-acyl group. Application of this type of reaction to some condensed pyrazine *N*-oxides is also described.

Irradiation of *N*-acetyl-2-methylthio-2′-nitrodiphenylamine (1a) (readily prepared from 2-acetamidophenyl

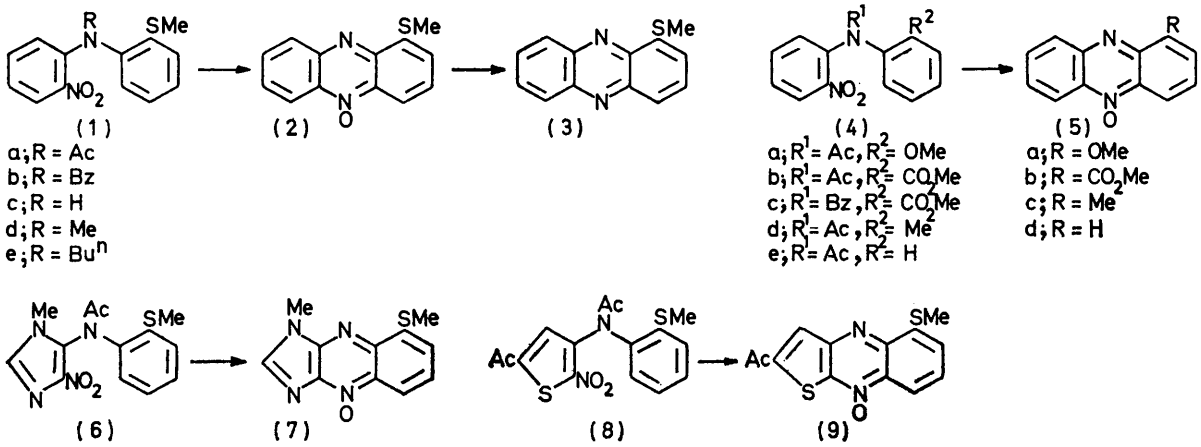
[1] Preliminary communication. Y Maki, T. Hosokami, and M. Suzuki, *J.C.S. Chem. Comm.*, 1972, 693.

[2] H. A. Morison, 'The Chemistry of Nitro and Nitroso Groups,' ed. H. Heuer, Wiley-Interscience, New York, Part 1, 1969, p. 165.

2-nitrophenyl sulphide *via* Smiles rearrangement and subsequent methylation [3]) in degassed benzene with a 100 W high-pressure mercury arc through a Pyrex filter gave 1-methylthiophenazine 5-oxide (2) in 50% yield [*m/e* 226 (*M* − O)]. Reduction of (2) with sodium hydrogen sulphite in aqueous methanol afforded 1-methylthiophenazine (3), identical with an authentic sample.[4] The position of the *N*-oxide function was confirmed by unequivocal synthesis of (2) from 2-nitro-2′-methylthiodiphenylamine (1c) by the procedure recently developed [5] in 5% yield. An improved yield of (2) (85%) was obtained when the *N*-benzoyl derivative (1b) was irradiated under analogous conditions.

The present photoconversion may represent a general synthesis of condensed pyrazine *N*-oxides. The nitroimidazole (6) and the nitrothiophen (8) were easily prepared by a combination of Smiles rearrangement and methylation from the corresponding sulphides (see Experimental section), and on irradiation in acetonitrile gave the imidazo[4,5-*b*]quinoxaline 4-oxide (7) and the thieno[2,3-*b*]quinoxaline 9-oxide (9) in 44 and 34% yields, respectively.

The effect of light of various wavelengths on the



SCHEME 1

In contrast, the parent amine (1c) and the *N*-alkyl compounds (1d and e) were unchanged even after prolonged irradiation. Thus, the photochemical formation of the *N*-oxide (2) occurs only when an *N*-acyl group is present.

Similarly, irradiation of the *N*-acyldiphenylamines (4a—c) in benzene or acetonitrile gave the corresponding phenazine *N*-oxides (5a and b) in moderate yields. 1-Methoxyphenazine 5-oxide (5a) was reduced with sodium hydrogen sulphite to the naturally occurring 1-methoxyphenazine.[6]

Irradiation of *N*-acetyl-2-nitrodiphenylamine (4e) and its 2′-methyl derivative (4d) in benzene, however, gave unsatisfactory results. The phenazine *N*-oxides (5d and c) were obtained only in poor yields, accompanied by some unidentified by-products. No formation of (5d) and (5c) was observed on prolonged irradiation. These results can be ascribed to further photoreaction of the initially formed *N*-oxides (5d and c). The phenazine *N*-oxide (5d) is known to undergo ready photoconversion into various types of compound.[7,8] A comparative photoreaction of compounds (5d) and (2) showed that the former is much more light-sensitive than the latter. Thus, yields of the phenazine *N*-oxides (2) and (5a—c) seem to depend on their stability to light.

photocyclisation was examined by use of a monochromator. The Table shows that irradiation at 311 nm is most efficient for the photoconversion of (4c) into (5b) in acetonitrile. The u.v. spectrum of (4c) in acetonitrile during this irradiation showed a gradual change with three isosbestic points at 252, 287, and 309 nm,

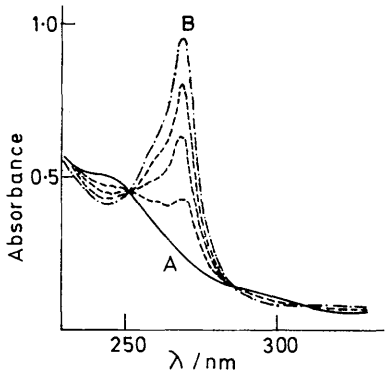
Effect of light of various wavelengths on the photochemical formation of 1-methoxycarbonylphenazine 5-oxide (5b)

Wavelength (nm) [a]	Yield (%) [b] of (5b)
232	11·0
258	25·2
285	49·6
311	66·9
338	65·8
364	48·4
391	27·1
417	14·6

[a] A JASCO GRM-FA radiating monochromator was used (light source 2 kW Xenon arc lamp). [b] Irradiation of (4c) was carried out in acetonitrile (10^{-3}M) for 30 min. Yields (%) were estimated by u.v. spectrophotometry and corrected on the basis of the energy distribution curve of the light source employed.

[3] W. J. Evans and S. Smiles, *J. Chem. Soc.*, 1935, 181.
[4] Y. Kidani and K. Ukai, *Chem. and Pharm. Bull.* (*Japan*), 1966, **14**, 293.
[5] B. Cross, D. J. Williams, and R. E. Woodall, *J. Chem. Soc.* (*C*), 1971, 2085.
[6] S. Yamagishi, Y. Koyama, Y. Fukakusa, Y. Komura, J. Ohashi, N. Hamamichi, and T. Arai, *J. Pharm. Soc. Japan*, 1971, **91**, 351.
[7] A. Albini, G. F. Bettenetti, and S. Pietra, *Tetrahedron Letters*, 1972, 3657.
[8] C. Kaneko, S. Yamada, and M. Ishikawa, *Tetrahedron Letters*, 1970, 2329.

indicating that the conversion proceeds quantitatively without competitive reactions (Figure).



U.v. spectral changes of the *N*-benzoyldiphenylamine (4c) in acetonitrile ($2·5 \times 10^{-6}$M) during irradiation with 311 nm light (at room temperature): A, (4c); B, 1-methoxycarbonylphenazine 5-oxide, (5b)

A possible mechanism for the present photocyclisation is outlined in Scheme 2. The addition of an excited nitro-group (n–π^* triplet) to an amide carbonyl C=O bond may form a cyclic or its equivalent diradical species [(B) or (B′)]. Subsequent collapse of (B) or (B′) with loss of an acyloxy-radical could lead to a radical (C) possessing a nitroso-function. The radical (C) could then undergo cyclisation followed by elimination of a hydrogen atom to give a phenazine *N*-oxide.

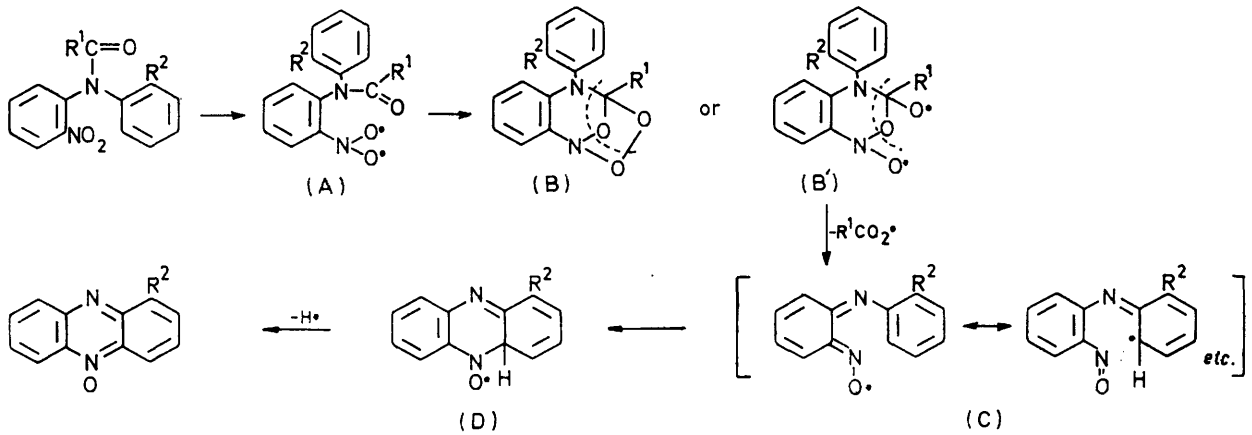
nitroso-group while an oxygen atom is apparently transferred to an *ortho*-substituent.[1] More recently, Amit and Patchornik [12] have reported that irradiation of *N*-acyl-2-nitrodiphenylamine (4e) readily gave the corresponding carboxylic acids, although they did not isolate phenazine *N*-oxide (5d) or its photolysis products. They also proved that the formation of the carboxylic acids involves transfer of an oxygen atom from the nitro-group to the *N*-acyl group on the basis of an ^{18}O-labelling experiment.

In view of these previous reports, we tentatively suggest the initial photoaddition of the nitro-group to the amide carbonyl group as the key step of the oxygen transfer.

Addition of benzophenone in various concentrations to the solution of (4b) did not suppress the photocyclisation leading to (5b) suggesting that the excited nitro-group reacting with an amide carbonyl group could be in the triplet state.

An acyloxy-radical formed as the result of fragmentation of the cyclic intermediate (B) or diradical (B′) was trapped as phenyl benzoate when the photoreaction of (4c) was conducted in benzene. Chromatography of the reaction mixture gave phenyl benzoate (4%) and benzoic acid (10%) as well as (5b). Under similar conditions, irradiation of benzoic acid in benzene did not give a detectable amount of phenyl benzoate (g.l.c.).

A reaction sequence comparable to the final two steps of our mechanism [(C) ⟶ (D) ⟶ *N*-oxides] may



SCHEME 2

The photoaddition of a nitro-group to the azomethine bond of a Schiff's base or a hydrazone has been suggested previously.[9,10] Recently, de Mayo, Charlton, and Liao have shown [11] that an n–π^* triplet state of an aromatic nitro-compound will undergo photocycloaddition to an alkene to give a 1,3,2-dioxazolidine in a stepwise fashion. A number of light-catalysed intramolecular rearrangements of nitroaromatic compounds are known in which the nitro-group is reduced to a

be involved in the oxidative cyclisation of 5-nitroso-6-anilinouracils leading to alloxazine *N*-oxides.[12]

EXPERIMENTAL

I.r. spectra were recorded with a Hitachi 215 spectrometer for potassium bromide discs and ^1H n.m.r. spectra with a Hitachi R-20B 60 MHz spectrometer for solutions in deuteriochloroform containing tetramethylsilane as internal standard. Mass spectra were measured at 75 eV with a JEOL JMS-O1SG spectrometer. All irradiations

[9] E. C. Taylor, B. Furth, and M. Pfan, *J. Amer. Chem. Soc.*, 1965, **87**, 1400.
[10] Y. Maki, M. Suzuki, and K. Izuta, *Tetrahedron Letters*, 1973, 147.
[11] J. L. Charlton, C. C. Liao, and P. De Mayo, *J. Amer. Chem. Soc.*, 1971, **93**, 2463.
[12] B. Amit and A. Patchornik, *Tetrahedron Letters*, 1973, 2205.

were performed with a Rikosha 100 W high-pressure mercury arc through a Pyrex filter under nitrogen. Reagent grade benzene and acetonitrile were redistilled prior to use as solvents. Column chromatography was performed on silica gel (Mallinckrodt; 100 mesh) with chloroform as eluant.

N-Benzoyl-2-methylthio-2'-nitrodiphenylamine (1b).—2-Methylthio-2'-nitrodiphenylamine (1c) (1·3 g) was dissolved in benzoyl chloride (8·6 g), and zinc chloride (0·5 g) was added with stirring. The mixture was then stirred overnight at room temperature and poured into water. The yellow solid was filtered off, washed with aqueous sodium hydrogen carbonate and water, dried, and recrystallised from acetone to give the N-*benzoyl derivative* (1b) (1·5 g, 83%) as yellow needles, m.p. 212—213° (Found: C, 66·15; H, 4·5; N, 7·75. $C_{20}H_{16}N_2O_3S$ requires C, 65·9; H, 4·45; N, 7·7%), $\nu_{max.}$ 1667 cm^{-1} (CO).

1-*Methylthiophenazine* 5-*Oxide* (2).—(a) *From the* N-*acetyldiphenylamine* (1a). A solution of the *N*-acetyl derivative (1a) [4] (1·6 g) in benzene (200 ml) was irradiated for 24 h, then concentrated under reduced pressure, and the residue was purified by chromatography and recrystallised from acetone to give the N-*oxide* (2) (0·65 g, 50%) as orange needles, m.p. 212—213° (Found: C, 64·7; H, 4·35; N, 11·35), *m/e* 242 (M^+) and 226 (M − 16), τ 1·2—2·7 (7H, m, ArH), and 7·39 (3H, s, SMe). $C_{13}H_{10}N_2OS$ requires C, 64·45; H, 4·15; N, 11·55%.

(b) *From the* N-*benzoyl derivative* (1b). A solution of the *N*-benzoyl derivative (1b) (1·8 g) in benzene (200 ml) was irradiated for 24 h, then concentrated under reduced pressure, and the residue was purified by chromatography and recrystallised from acetone to give the *N*-oxide (2) (1·0 g, 85%) as orange needles, m.p. 212—213°, identical (i.r. spectrum) with the specimen obtained in (a).

Reduction of 1-*Methylthiophenazine* 5-*Oxide* (2) *with Sodium Hydrogen Sulphite.*—Sodium hydrogen sulphite (60 mg) was added to a stirred suspension of the *N*-oxide (2) (20 mg) in 70% aqueous methanol (20 ml). The mixture was then stirred at room temperature for 4 h, concentrated under reduced pressure, and extracted with chloroform. Material from the dried extract was purified by chromatography and recrystallised from ethanol to give 1-methylthiophenazine (3) (7 mg, 38%) as yellow needles, m.p. 172° (lit.,[4] 172—173°), identical (i.r. spectrum) with an authentic specimen.

N-Acetyl-2-methoxy-2'nitrodiphenylamine (4a).—2-Methoxy-2'-nitrodiphenylamine (1·0 g) was dissolved in acetic anhydride (5·0 g), and zinc chloride (0·5 g) was added with stirring. The mixture was then stirred overnight at room temperature and poured into water. The brown solid, was filtered off, washed with water, dried, and recrystallised from ethanol to give the N-*acetyl derivative* (4a) (0·9 g, 77%) as pale yellow plates, m.p. 104—105° (Found: C, 63·2; H, 5·0; N, 9·95. $C_{15}H_{14}N_2O_4$ requires C, 62·95; H, 4·95; N, 9·8%), $\nu_{max.}$ 1680 cm^{-1} (CO), τ 2·0—3·2 (8H, m, ArH), 6·05 (3H, s, OMe), and 8·02 (3H, s, COMe).

1-*Methoxyphenazine* 5-*Oxide* (5a).—A solution of the *N*-acetyl derivative (4a) (0·7 g) in acetonitrile (170 ml) was irradiated for 6 h, then concentrated. The oily residue was chromatographed to separate the unchanged *N*-acetyl derivative (4a) (0·1 g, 14%) and another crystalline mass. The latter was recrystallised from ether to give the N-*oxide* (5a) (0·23 g, 42%) as yellow needles, m.p. 207—208° (Found: C, 69·2; H, 4·45; N, 12·3. $C_{13}H_{10}N_2O_2$ requires C, 69·0; H, 4·45; N, 12·4%), *m/e* 226 (M^+) and 210 (M − 16), τ 1·1—3·0 (7H, m, ArH) and 5·80 (3H, s, OMe). As described for the *N*-oxide (2), the *N*-oxide (5a) was reduced with sodium hydrogen sulphite to give 1-methoxyphenazine (57%) as yellow needles, m.p. 170—171° (lit.,[6] 170—171°), identical (i.r. spectrum) with an authentic specimen.

N-Acetyl- and N-Benzoyl-2-methoxycarbonyl-2'-nitrodiphenylamine (4b and c).—A solution of 2-carboxy-2'-nitrodiphenylamine (2·0 g) in absolute methanol (30 ml) containing concentrated sulphuric acid (2 ml) was refluxed for 5 h. The residue obtained by evaporation was extracted with chloroform after neutralisation with aqueous 10% sodium carbonate. The extract was washed with water, dried, and evaporated. The residue was recrystallised from methanol to give the *methyl ester* (1·6 g, 76%) as orange needles, m.p. 159—160° (Found: C, 61·95; H, 4·55; N, 10·35. $C_{14}H_{12}N_2O_4$ requires C, 61·75; H, 4·45; N, 10·3%), $\nu_{max.}$ 3300 and 1690 cm^{-1} (NH and CO), τ −1·13 (1H, s, NH), 1·7—3·2 (8H, m, ArH), and 6·03 (3H, s, CO_2Me).

To the methyl ester (2·0 g) dissolved in acetic anhydride (20 ml) zinc chloride (1·0 g) was added. The mixture was then stirred at 50° for 3 h, concentrated under reduced pressure, and extracted with chloroform. The extract was washed with water, dried, and evaporated to dryness. The residue was recrystallised from petroleum (b.p. 30—70°) to give the N-*acetyl derivative* (4b) (2·1 g, 91%) as prisms, m.p. 109—111° (Found: C, 61·05; H, 4·45; N, 8·85. $C_{16}H_{14}N_2O_5$ requires C, 61·15; H, 4·5; N, 8·9%), $\nu_{max.}$ 1715 and 1660 cm^{-1} (CO), τ 1·7—3·0 (8H, m, ArH), 6·04 (3H, s, CO_2Me), and 8·05 (3H, s, COMe).

The N-*benzoyl derivative* (4c), prepared from the methyl ester in a similar manner to (1b) in 63% yield, formed yellow prisms, m.p. 155—156° (Found: C, 67·15; H, 4·45; N, 7·5. $C_{21}H_{16}N_2O_5$ requires C, 67·0; H, 4·3; N, 7·45%), $\nu_{max.}$ 1710 and 1660 cm^{-1} (CO), τ 1·8—3·0 (13H, m, ArH) and 6·22 (3H, s, CO_2Me).

1-*Methoxycarbonylphenazine* 5-*Oxide* (5b).—(a) *From the* N-*benzoyl derivative* (4c). A solution of the *N*-benzoyl derivative (4c) (0·94 g) in benzene (170 ml) was irradiated for 6 h, then concentrated under reduced pressure; the residue was purified by chromatography and recrystallised from hexane to give the N-*oxide* (5b) (0·06 g, 9%) as yellow needles, m.p. 135° (Found: C, 66·45; H, 3·95; N, 10·7. $C_{14}H_{10}N_2O_3$ requires C, 66·15; H, 3·95; N, 11·0%), *m/e* 254 (M^+), 238 (M − 16), 223 (M − OMe), and 195 (M − CO_2Me), $\nu_{max.}$ 1710 cm^{-1} (CO), τ 1·0—2·5 (7H, m, ArH), and 5·83 (3H, s, CO_2Me). An improved yield (61%) was obtained by use of acetonitrile as solvent.

(b) *From the* N-*acetyl derivative* (4b). A solution of the *N*-acetyl derivative (0·9 g) in acetonitrile (170 ml) was irradiated for 6 h, then concentrated. The oily residue was chromatographed to separate the unchanged *N*-acetyl derivative (4b) (0·15 g, 17%) and another crystalline mass. The latter was recrystallised from hexane to give the *N*-oxide (5b) (0·34 g, 55%) as yellow needles, m.p. 134—135°, identical (i.r. spectrum) with the sample obtained in (a).

The *N*-oxide (5b) was reduced to methyl phenazine-1-carboxylate as in the case of the *N*-oxide (2). The ester, m.p. 127°, was identical with an authentic sample.[6]

N-Acetyl-2-methyl-2'-nitrodiphenylamine (4d).—To a solution of 2-methyl-2'-nitrodiphenylamine (1·14 g) in acetic anhydride (5 ml), zinc chloride (0·2 g) was added. The mixture was then heated on a water-bath for 1 h, concentrated under reduced pressure, and extracted with

chloroform. The extract was washed with water, dried, and evaporated to dryness. The residue was recrystallised from ethanol to give the N-*acetyl derivative* (4d) (0·9 g, 66%) as yellow prisms, m.p. 94—95° (Found: C, 66·2; H, 5·25; N, 10·0. $C_{15}H_{14}N_2O_3$ requires C, 66·65; H, 5·2; N, 10·35%), $\nu_{max.}$ 1660 cm^{-1} (CO).

Photochemical Formation of 1-*Methylphenazine* 5-*Oxide* (5c).—A solution of the *N*-acetyl derivative (4d) (0·5 g) in acetonitrile (200 ml) was irradiated for 12 h, then concentrated under reduced pressure. The oily residue was chromatographed to separate a crystalline mass and an oily fraction containing several unidentified products. The former was recrystallised from hexane to give 1-*methylphenazine* 5-*oxide* (5c) (11 mg, 3%) as needles, m.p. 175° (Found: C, 73·8; H, 4·75; N, 13·1. $C_{13}H_{10}N_2O$ requires C, 74·25; H, 4·8; N, 13·35%), *m/e* 210 (M^+) and 194 (M − 16).

Analogously, phenazine 1-oxide (5d) was obtained from *N*-acetyl-2-nitrodiphenylamine (4d) only in 5% yield.

1-*Methyl*-5-[N-(2-*methylthiophenyl*)*acetamido*]-4-*nitroimidazole* (6).—2-Aminobenzenethiol (4·2 g) was dissolved in ethanolic sodium ethoxide (1·1 g of sodium in 100 ml of ethanol). To this stirred solution was added 5-chloro-1-methyl-4-nitroimidazole [13] (5 g) and the mixture was stirred at room temperature for 3 h. The orange crystals were collected, washed with water, dried, and recrystallised from methanol to give 5-(2-*aminophenylthio*)-1-*methyl*-4-*nitroimidazole* (4·8 g) as orange prisms, m.p. 129—130° (Found: C, 48·15; H, 4·1; N, 22·3. $C_{10}H_{10}N_4O_2$ requires C, 48·0; H, 4·05; N, 22·4%), $\nu_{max.}$ 3450 and 3350 cm^{-1} (NH_2).

To a solution of the sulphide (5·6 g) in pyridine (20 ml) was added acetic anhydride (16 ml). The mixture was set aside overnight, then poured into water (200 ml). The pale yellow crystals were separated, washed with water, dried, and recrystallised from methanol to give an N-*acetyl derivative* (5·2 g) as pale yellow needles, m.p. 165—166° (Found: C, 49·55; H, 4·45; N, 19·0. $C_{12}H_{12}N_4O_3S$ requires C, 49·3; H, 4·15; N, 19·15%), $\nu_{max.}$ 3320 and 1680 cm^{-1} (NH and CO).

To a solution of the *N*-acetyl derivative (1·4 g) and methyl iodide (1 ml) in acetone (150 ml) under reflux was added aqueous potassium hydroxide (0·8 g in 4 ml). After 15 min refluxing more methyl iodide (2 ml) was added and the solvent was evaporated off. The residue was washed with water, dried, and recrystallised from methanol to give *compound* (6) (1·1 g) as pale yellow prisms, m.p. 182—183° (Found: C, 51·2; H, 4·85; N, 18·35. $C_{13}H_{14}N_4O_3S$ requires C, 50·95; H, 4·6; N, 18·3%), $\nu_{max.}$ 1710 cm^{-1} (CO), τ 2·5—3·0 (5H, m, ArH), 6·43 (3H, s, NMe), 7·48 (3H, s, SMe), and 7·83 (3H, s, COMe).

1-*Methyl*-8-*methylthio*-1H-*imidazo*[4,5-b]*quinoxaline* 4-*Oxide* (7).—A solution of the *N*-acetyl derivative (6) (0·025M) in acetonitrile was irradiated for 3 h. The separated yellow crystals were collected and recrystallised from acetone to give the N-*oxide* (7) (44%) as yellow needles, m.p. 295—296° (decomp.) (Found: C, 53·65; H, 4·0; N, 22·95. $C_{11}H_{10}N_4OS$ requires C, 53·65; H, 4·1; N, 22·75%), *m/e* 246 (M^+, base peak) and 230 (M − 16).

The *N*-oxide (7) was reduced with sodium hydrogen sulphite in aqueous methanol (reflux for 3 h). 1-*Methyl*-8-*methylthio*-1H-*imidazo*[4,5-b]*quinoxaline*, m.p. 285—286°, was obtained in 60% yield (Found: C, 57·25; H, 4·35; N, 24·1. $C_{11}H_{10}N_4S$ requires C, 57·35; H, 4·35; N, 24·35%), *m/e* 230 (M^+) and 215 (M − Me), τ 1·35 (1H, s, 2-H), 2·7—3·5 (3H, m, ArH), 6·90 (3H, s, NMe), and 7·58 (3H, s, SMe).

5-*Acetyl*-3-[N-(2-*methylthiophenyl*)*acetamido*]-2-*nitrothiophen* (8).—2-Aminobenzenethiol (1 g) was dissolved in methanolic sodium hydroxide (0·4 g, 12 ml). After addition of 5-acetyl-3-bromo-2-nitrothiophen (2 g),[14] the mixture was stirred at room temperature for 2 h. The yellow crystals were collected, washed with water, and dried to give 5-*acetyl*-3-(2-*aminophenylthio*)-2-*nitrothiophen* (2·3 g), m.p. 165—167° (Found: C, 48·85; H, 3·7; N, 9·3. $C_{12}H_{10}N_2O_3S_2$ requires C, 48·95; H, 3·4; N, 9·5%), $\nu_{max.}$ 3430, 3350, and 1640 cm^{-1} (NH_2 and CO).

To a solution of the sulphide (1·9 g) in pyridine (4 ml) was added acetic anhydride (3·1 g). The mixture was set aside overnight, then poured into water. The yellow crystals were collected, washed with water, dried, and recrystallised from acetone to give an N-*acetyl derivative* (1·8 g) as pale yellow needles, m.p. 214—215° (Found: C, 50·1; H, 3·6; N, 8·3. $C_{14}H_{12}N_2O_4S_2$ requires C, 50·0; H, 3·6; N, 8·35%), $\nu_{max.}$ 3250 and 1650 cm^{-1} (NH and CO).

To a solution of the *N*-acetyl derivative (2 g) and methyl iodide in methanol–acetone (1 : 2; 60 ml) under reflux was added methanolic potassium hydroxide (1·6 g in 16 ml). After refluxing for 20 min, more methyl iodide (3 ml) was added and the solvent was evaporated off. The crystalline residue was washed with water, dried, and recrystallised from ethanol to give *compound* (8) (1·2 g) as pale yellow prisms, m.p. 143—145° (Found: C, 52·85; H, 4·2; N, 8·3. $C_{15}H_{14}N_2O_4S_2$ requires C, 52·95; H, 4·15; N, 8·25%), $\nu_{max.}$ 1700 and 1660 cm^{-1} (CO), τ 1·92 (1H, s, 4-H), 2·4—2·8 (3H, m, ArH), and 7·45 (6H, s, SMe and COMe).

2-*Acetyl*-5-*methylthiothieno*[2,3-b]*quinoxaline* 9-*Oxide* (9).—A solution of the *N*-acetyl derivative (8) (0·01M) in acetonitrile was irradiated for 5 h, then concentrated under reduced pressure, and the residue was purified by silica-gel chromatography and recrystallised from acetone to give the N-*oxide* (9) (34%) as red needles, m.p. 228—230° (decomp.) (Found: C, 53·65; H, 3·45; N, 9·35. $C_{13}H_{10}N_2O_2S_2$ requires C, 53·75; H, 3·5; N, 9·65%), *m/e* 290 (M^+), and 274 (M − 16), $\nu_{max.}$ 1660 cm^{-1} (CO).

[3/2544 *Received*, 14*th December*, 1973]

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[14] J. Sarasin and E. Wagmann, *Helv. Chim. Acta*, 1924, **7**, 713.