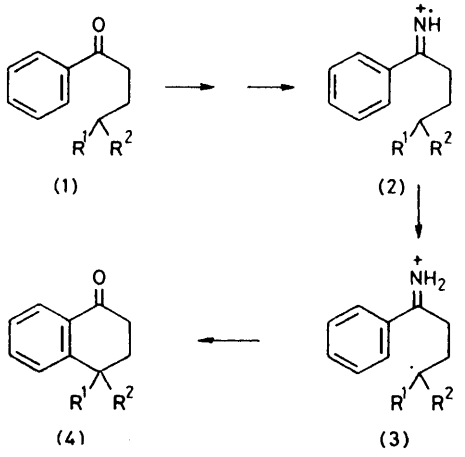
Iminyls. Part 7.[1] Intramolecular Hydrogen Abstraction; Synthesis of Heterocyclic Analogues of α-Tetralone

By **Alexander R. Forrester,* Russell J. Napier,** and **Ronald H. Thomson,** Chemistry Department, University of Aberdeen, Aberdeen AB9 2UE, Scotland

A series of alkyl (C_4 or greater) heteroaryl iminyls have been generated by oxidation of the corresponding oxime-*O*-acetic acids with persulphate. These react to give fused heteroaryl cyclohexanones.

PREVIOUSLY we described [2] a new synthesis of tetralones (4) from alkyl aryl ketones (1) in which the latter were converted into iminyl radicals. After protonation (2) these abstracted γ-hydrogen from the alkyl chain giving C-radicals (3), which cyclised onto the benzene ring

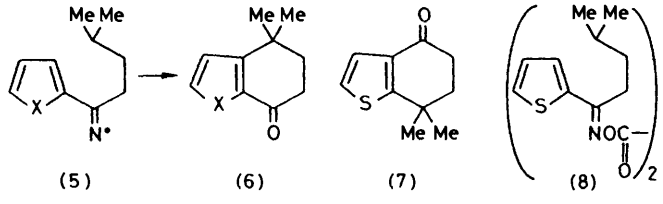


[(3) ⟶ (4)]. The scope of this procedure has now been widened to include preparation of several new heterocyclic analogues of (4).

RESULTS AND DISCUSSION

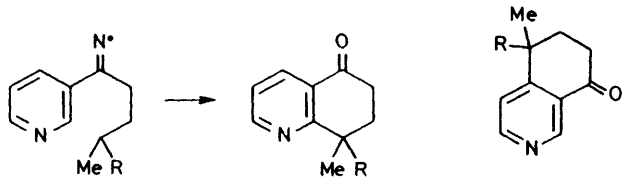
The iminyls were generated by oxidation of the corresponding oxime-*O*-acetic acids with persulphate in boiling aqueous solution.[3] The yields of products are collected in Table 1.

Thienyl and Furyl Iminyls.—2-Thienyl and 2-furyl iminyls (5; X = S and O, respectively) yielded the corresponding heteroaryl ketones (6; X = S and O) in



44—59% yield with no evidence of significant attack by the sulphate radical-anion (or hydroxyl radical) on the heteroaryl nucleus. Since the analogous 3-thienyl iminyl gave a similar yield of (7) it appears that intramolecular homolytic alkylation occurs with equal facility at positions 2 or 3 of the thiophen nucleus. In contrast intermolecular homolytic substitution [4] occurs predominantly at position 2. The importance [2] of acidic conditions in these conversions which ensures equilibrium concentrations of the reactive imminium radical cation ($R_2C{=}\overset{+}{N}H$) was illustrated by two separate experiments: (*i*) when the 2-thienyl iminyl (5; X = S) was generated in a solution of pH 6.2, rather than the usual pH 3.0—3.5, the yield of cyclised product decreased to 16%; (*ii*) when the 2-thienyl iminyl was generated by photolysis of the oxalate [3] (8) the cyclic ketone (6; X = S) was produced only when the photolysis solution included trifluoroacetic acid.

Pyridinyl Iminyls.—Homolytic intermolecular alkylation of pyridine under neutral conditions gives significant amounts of all three isomeric mono-alkyl pyridines; [5] the ratio of 4-isomer to 2-isomer is usually in the range 1 : 3—4. In acidic solution [5,6] only the 2- and 4-isomers are formed, the ratio being in the range 2—4 : 1. When the iminyl (9; R = Me) was generated at pH 3.0—3.5 the ratio of 4- to 2-cyclisation to give (11) and (10), respectively, was *ca.* 1 : 1. Raising the pH to 5.0—6.0 decreased this ratio to 1 : 1.5, while at pH 1.5 it increased to 3.7 : 1. Hence an increase in the relative yield of the 4-isomer



with decrease in pH occurs for both the intra- and intermolecular reactions. Interestingly, 2-phenylethylation of 3-methoxycarbonylpyridine in acidic solution, a close intermolecular analogue of the conversion (9) ⟶ (10) + (11), gave a reactivity ratio of 3.05 : 1 for the 4- and 2-positions.[7] As in the benzene series, overall yields of cyclised products were lower when the iminium radical cation had to abstract a secondary hydrogen atom from the alkyl chain, *e.g.* with (9; R = H). Nevertheless the relative reactivity of the 2- and 4-positions at the cyclisation step was still *ca.* 1 : 1. Intermolecular homolytic alkylation at the 3-position of pyridine is a poor reaction [5,6] and the intramolecular reaction appears to be similar. Thus, the iminyl (12) gave only small amounts of the heteroarylketone (13).

The substitution patterns of the heteroaryl ketones (10), (11), and (13) were easily established by n.m.r. measurements (Experimental section).

(12) (13)

EXPERIMENTAL

I.r. spectra were measured as KBr discs (solids) or thin films (liquids) and n.m.r. spectra in deuteriochloroform unless stated otherwise. Petrol refers to light petroleum, b.p. 60—80 °C. Merck silica gel GF_{254} or HF_{254} was used for chromatographic separations.

Preparation of Starting Materials.—Alkyl heteroaryl ketones and their oximes. The following ketones were prepared by treatment of the appropriate heteroaryl nitrile (1 mol) with alkylmagnesium bromide [3] (1 mol). They

Yields (%) of products from alkyl heteroaryl iminyls $ArC(=\dot{N}H)R$ (14)

Ar	R	pH	Yield (%) and product:
2-Thienyl	$CH_2CH_2CHMe_2$	6.2	*ca.* 16 (6; X = S) [c]
		4.5	44 (6; X = S); 62 (X = S) [b]
		1.5	36 (6; X = S) [c]
3-Thienyl	$CH_2CH_2CHMe_2$	3.0—3.5	49 (X = S)
2-Thienyl	$CH_2CH_2CHMe_2$		15 (X = S) [d]
2-Furyl	$CH_2CH_2CHMe_2$	3.0—3.5	59 (X = O)
3-Pyridinyl	$CH_2CH_2CHMe_2$	3.0—3.5	42 (10; R = Me); [a] 37 (11; R = Me) [a] 27 (10; R = Me); 22 (11; R = Me)
		3.0—6.0	28 (10; R = Me); [a] 18 (11; R = Me) [a]
		1.5	10 (10; R = Me;) [a] 38 (11; R = Me) [a]
3-Pyridinyl	$CH_2CH_2CH_2Me$	3.0—3.5	18 (10; R = H); 12 (11; R = H)
4-Pyridinyl	$CH_2CH_2CH_2Me$	3.0—3.5	*ca.* 5 (13)

[a] Yield based on g.l.c. measurements. [b] 2 Mol persulphate used. [c] Aqueous acetonitrile used as solvent. [d] Iminyl generated from oxalate.

were converted into the corresponding oximes in the usual way. 1-(4'-Pyridyl)pentan-1-one [8] (76%) was an oil, (b.p. 90—95 °C/0.2 mmHg) (Found: C, 73.3; H, 8.0; N, 8.5%. M^+, 163.099 8. Calc. for $C_{10}H_{13}NO$: C, 73.6; H, 8.0; N, 8.6%; *M*, 163.099 7); $\lambda_{max.}$ 230 and 281 nm (log ε 3.32, 3.48); $\nu_{max.}$ 1 690 cm^{-1}; δ 0.95 (3 H, t, *J* 7 Hz, Me), 1.5 (4 H, m, CH_2CH_2), 3.0 (2 H, t, *J* 7 Hz, CH_2), 7.7 (2 H, dd, *J* 6 and 1.5 Hz, Ar-H), and 8.75 (2 H, dd, *J* 6 and 1.5 Hz, Ar-H). Its *oxime* had m.p. 92—93.5 °C (from chloroform–petrol) (Found: C, 67.4; H, 7.7; N, 15.4. $C_{10}H_{14}N_2O$ requires C, 67.4; H, 7.9; N, 15.7%). 1-(3-*Pyridyl*)-4-*methylpentan*-1-*one* (68%) was an oil (b.p. 115—118 °C/0.075 mmHg) (Found: C, 74.8; H, 8.7; N, 7.8%; M^+, 177.114 9. $C_{11}H_{15}NO$ requires C, 74.5; H, 8.5; N, 7.9%; *M*, 177.115 4); $\lambda_{max.}$ 238 and 268 nm (log ε 3.59, 3.40); $\nu_{max.}$ 1 690 cm^{-1}; δ 0.95 (6 H, d, *J* 5 Hz, Me_2), 1.65 (3 H, m, CH_2CH), 3.0 (2 H, t, *J* 7 Hz, CH_2), and 7.4, 8.2, 8.75, 9.15 (each 1 H, m, Ar-H). Its *oxime* had m.p. 85—87 °C (from chloroform–petrol) (Found: C, 68.9; H, 8.5; N, 14.6. $C_{11}H_{16}N_2O$ requires C, 68.7; H, 8.4; N, 14.6%). 1-(3'-Pyridyl)-pentan-1-one [9] (64%) was an oil (b.p. 95—105 °C/0.05 mmHg). Its oxime had m.p. 77—78.5 °C (Found: C, 67.7; H, 7.9; N, 15.4%; M^+, 178.110 8. Calc. for $C_{10}H_{14}N_2O$: C, 67.4; H, 7.9; N, 15.7%; *M*, 178.110 6); $\nu_{max.}$ 1 690 cm^{-1}; δ 1.0—1.5 (7 H, m, $MeCH_2CH_2$), 3.0 (2 H, t, *J* 7 Hz, CH_2), and 7.4, 8.25, 8.8, 9.2 (each 1 H, m, Ar-H). 1-(2-Thienyl)-4-methylpentan-1-one [10] (60%) was an oil (b.p. 89—91 °C/0.08 mmHg) (Found: C, 65.8; H, 7.7%; M^+, 182.076 3. Calc. for $C_{10}H_{14}OS$: C, 65.9; H, 7.4%. *M*, 182.076 6); $\lambda_{max.}$ 212.5, 261, 285 nm (log ε 2.94, 3.97, 3.88); $\nu_{max.}$ 1 655 cm^{-1}; δ 0.95 (6 H, d, *J* 5 Hz, $CHMe_2$), *ca.* 1.65 (3 H, m, CH_2CH), 2.9 (2 H, t, *J* 8 Hz, CH_2) 7.1 (1 H, m, 4-ArH), and 7.7 (2 H, m, 3,5-Ar-H). Its *oxime* had m.p. 88.5—90.5 °C (from chloroform–petrol) (Found: C, 60.5; H, 7.8: N, 7.5. $C_{10}H_{15}NOS$ requires C, 60.9; H, 7.7; N, 7.1%). 1-(3-*Thienyl*)-4-*methylpentan*-1-*one* (31%) was an oil (b.p. 69—71 °C/0.05—0.1 mmHg) (Found: C, 65.6; H, 7.6; S, 17.4%; M^+, 182.076 7. $C_{10}H_{15}OS$ requires C, 65.9; H, 7.4; S, 17.7%; *M*, 182.076 6); $\lambda_{max.}$ 212 and 250 nm log ε 4.12, 4.03); $\nu_{max.}$ 1 680 cm^{-1}; δ 0.95 (6 H, d, *J* 5 Hz, Me_2), 1.65 (3 H, m, $CHCH_2$), 2.9 (2 H, t, *J* 7 Hz, CH_2), 7.3, 7.55 (each 1 H, m, Ar-H), and 8.08 (1 H, m, 2-Ar-H). 1-(2-Furyl)-4-methylpentan-1-one [11] (80%) was an oil (b.p. 50 °C/0.1 mmHg) (Found: C, 72.2; H, 8.3. Calc. for $C_{10}H_{14}O_2$: C, 72.6; H, 8.5%); $\lambda_{max.}$ 226, 271 (log ε 3.40, 4.11); $\nu_{max.}$ 1 665 cm^{-1}; δ 0.95 (6 H, d, *J* 5 Hz, Me_2), 1.6 (3 H, m, CH_2CH), 2.82 (2 H, t, *J* 8 Hz, CH_2), 6.6 (1 H, m, Ar-H), 7.25 (1 H, d, *J* 3 Hz, Ar-H), and 7.65 (1 H, m, Ar-H).

Preparation of Imino-oxyacetic Acids.—These were prepared from (*a*) the corresponding oxime, bromoacetic acid, and alkali;[3] (*b*) the corresponding ketone, amino-oxyacetic acid hydrochloride, and alkali; [3] and (*c*) hydrolysis of the corresponding imino-oxyacetic ester with sulphuric acid, the ester being prepared from the salt of the oxime [12] and ethyl bromoacetate.

4-*Methyl*-1-(2-*thienyl*)*pentylideneamino-oxyacetic acid* [method (*a*), 75%] had m.p. 43.5—46 °C (from hexane) (Found: C 56.8; H 6.7; N 5.5; S, 12.8%; M^+, 255.092 8. $C_{12}H_{17}NO_3S$ requires C, 56.5; H, 6.7; N, 5.5; S, 12.6%; *M*, 225.092 8); $\nu_{max.}$ 3 400 and 1 730 cm^{-1}; δ 0.95 (6 H, d, *J* 6 Hz, Me_2), 1.65 (3 H, m, CH_2CH), 2.75 (2 H, br t, *J* 8 Hz, CH_2), 4.7, 4.8, (1 H, s, OCH_2), and 6.95—7.6 (3 H, m, Ar-H). 4-*Methyl*-1-(2-*furyl*)*pentylideneamino-oxyacetic acid* [method (*b*), 87%] had m.p. 63.5—65.5 °C (from hexane) (Found: C, 60.4; H, 7.4; N, 5.9%; M^+, 239.115 5. $C_{12}H_{17}NO_4$ requires C, 60.2; H, 7.2; N, 5.9; *M*, 239.115 7); $\nu_{max.}$ 3 400 and 1 730 cm^{-1}; δ 0.9 (6 H, d, *J* 5 Hz, Me_2), 1.5 (3 H, m, CH_2CH), 2.65 (2 H, br t, *J* 8 Hz, CH_2), 4.75 (2 H, s, OCH_2), and 6.5—7.5 (3 H, m, Ar-H). 4-*Methyl*-1-(3-*thienyl*)*pentylideneamino-oxyacetic acid* [method (*b*), 50%] had m.p. 70—72 °C (from hexane) (Found: C, 56.4; H 6.5; N, 5.6; S, 12.7%; M^+, 255.093 1. $C_{12}H_{17}NO_3S$ requires C, 56.5; H, 6.7; N, 5.5; S, 12.6%; *M*, 255.093 1); $\nu_{max.}$ 3 440 and 1 725—1 715 cm^{-1}; δ 0.9 (6 H, d, *J* 6 Hz, Me_2), 1.5 (3 H, m, CH_2CH), 2.75 (2 H, t, *J* 8 Hz, CH_2), 4.7 (2 H, s, OCH_2), and *ca.* 7.3 (3 H, m, Ar-H).

Ethyl 4-*methyl*-1-(3-*pyridyl*)*pentylideneamino-oxyacetate* [method (*c*)] was an oil (b.p. 130—135 °C/0.075 mmHg) (Found: C, 64.8; H, 7.8; N, 9.8%; M^+, 278.163 2. $C_{15}H_{22}N_2O_3$ requires C, 64.7; H, 8.0; N, 10.1%; *M*, 278.163 0); $\nu_{max.}$ 1 760 cm^{-1}; δ 0.95 (6 H, d, *J* 5 Hz, Me_2), 1.3 (3 H, t, *J* 7 Hz, Me), 1.5 (3 H, m, CH_2CH), 2.8 (2 H, t, *J*

8 Hz, CH_2), 4.2 (2 H, q, *J* 7 Hz, CH_2), 4.7 (2 H, s, OCH_2), 7.3 (1 H, m, 5-Ar-H), 7.9 (1 H, m, 4-Ar-H), 8.6 (1 H, m, 6-Ar-H), and 8.85 (1 H, m, 2-Ar-H). Hydrolysis of this ester by refluxing with 0.5M sulphuric acid gave 4-methyl-1-(3-pyridyl)pentylideneamino-oxyacetic acid as a hygroscopic powder * (estimated purity 86% by n.m.r. comparison with piperonal); $\nu_{max.}$ 3 485—3 208 and 1 600 cm^{-1}; δ(CD_3OD) 0.95 (6 H, d, *J* 6 Hz, Me_2), *ca.* 1.4 (3 H, m, CH_2CH), 2.9 (2 H, br t, *J* 8 Hz, CH_2), 4.6 and 4.8 (2 H, each s, OCH_2), 8.2 (1 H, m, 5-Ar-H), and *ca.* 9.0 (3 H, m, Ar-H). This material was used for the persulphate oxidations. *Methyl (4-pyridyl)pentylideneamino-oxyacetate* was an oil (b.p. 110—120 °C/0.15 mmHg) (Found: C, 62.3; H, 7.1; N, 11.0%; M^+, 250.131 3. $C_{13}H_{18}N_2O_3$ requires C, 62.4; H, 7.25; N, 11.2%; *M*, 250.131 7); $\nu_{max.}$ 1 735 cm^{-1}; δ 0.95 (3 H, t, *J* 7 Hz, Me), *ca.* 1.5 (4 H, m, CH_2CH_2), 2.8 (2 H, t, *J* 8 Hz, CH_2), 3.75 (3 H, s, OMe), 4.75 (2 H, s, OCH_2), 7.5 (2 H, m, Ar-H), and 8.6 (2 H, m, Ar-H). Hydrolysis of this ester gave 1-(4-pyridyl)pentylideneamino-oxyacetic acid as a powder * (estimated purity 86% by n.m.r. comparison with piperonal); $\nu_{max.}$ 3 420 and 1 620 cm^{-1}; δ(CD_3OD) 0.95 (3 H, br t, Me), 1.55 (4 H, m, CH_2CH_2), 2.90 (2 H, t, *J* 7 Hz, CH_2), 4.81 (2 H, s, OCH_2), 7.75 (2 H, dd, *J* 6 and 2 Hz, ArH), and 8.6 (2 H, dd, *J* 6 and 2 Hz, ArH).

1-(3-*Pyridyl*)*pentylideneamino-oxyacetic acid* [method (*b*)] was a thick oil † (estimated purity 83% by n.m.r. comparison with piperonal) (Found: $M^+ - C_2H_3O_3$, 161.107 9. $C_{10}H_{13}N_2$ requires *M*, 161.107 8); $\nu_{max.}$ 3 500—3 200 and 1 620 cm^{-1}; δ(CD_3OD) 0.95 (3 H, br t, *J* 7 Hz, CH_3), 1.5 (4 H, m, CH_2CH_2), 2.9 (2 H, br t, *J* 8 Hz, CH_2), 4.6 (2 H, s, OCH_2), 7.5 (1 H, m, 5-Ar-H), 8.1 (1 H, m, 4-Ar-H), 8.6 (1 H, m, 6-Ar-H), and 8.85 (1 H, br s, 2-Ar-H).

Oxidations with Persulphate.—To a solution of the oxyacetic acid (0.01 mol) in 0.1M sodium hydroxide solution (110 ml, 0.011 mol) under reflux a solution of potassium persulphate (0.015 mol) in water was added dropwise. Heating was continued until either the solution darkened or precipitation was complete (*ca.* 5—15 min). The mixture was cooled and extracted into ether. The ethereal extracts were extracted with 2M alkali and then dried. The residue obtained on removal of solvent was either crystallised or chromatographed on silica (p.l.c.).

(*i*) 4-Methyl-1-(2-thienyl)pentylideneamino-oxyacetic acid gave 4,4-*dimethyl*-4,5,6,7-*tetrahydrobenzo*[b]*thiophen*-7-*one* (44%), m.p. 43.5—45.5 °C (from chloroform–petrol) (Found: C, 66.5; H, 7.0; S, 17.4%; M^+, 180.060 7. $C_{10}H_{12}OS$ requires C, 66.6; H, 6.7; S, 17.8%; *M*, 180.060 6); $\lambda_{max.}$ 208 and 273 nm (log ε 3.28, 4.05); $\nu_{max.}$ 1 660 cm^{-1}; δ 1.37 (6 H, s, Me_2), 2.05 (2 H, t, *J* 7 Hz, CH_2), 2.73 (2 H, t, *J* 7 Hz, CH_2), 7.1 (1 H, d, *J* 5 Hz, Ar-H), and 7.65 (1 H, d, *J* 5 Hz, Ar-H).

(*ii*) 4-Methyl-1-(3-thienyl)pentylideneamino-oxyacetic acid gave 7,7-*dimethyl*-4,5,6,7-*tetrahydrobenzo*[b]*thiophen*-4-*one* (49%) as a pale yellow oil (b.p. 55—60 °C/0.2 mmHg) (Found: C, 66.8; H, 6.7; S, 17.8%; M^+, 180.060 6. $C_{10}H_{12}OS$ requires C, 66.6; H, 6.7; S, 17.8%; *M*, 180.060 6); $\lambda_{max.}$ 220 and 254 nm (log ε 4.12, 4.06); $\nu_{max.}$ 1 670 cm^{-1}; δ 1.45 (6 H, s, Me_2), 2.05 (2 H, t, *J* 7 Hz, CH_2), 2.65 (2 H, t, *J* 7 Hz, CH_2), 7.08 (1 H, d, *J* 5 Hz, Ar-H), and 7.37 (1 H, d, *J* 5 Hz, Ar-H).

(*iii*) 4-Methyl-1-(2-furyl)pentylideneamino-oxyacetic acid gave 4,4-*dimethyl*-4,5,6,7-*tetrahydrobenzo*[b]*furan*-7-*one* (59%), m.p. 73—75.5 °C (sublimation) (Found: C, 72.9; H, 7.4%; M^+, 164.083 6. $C_{10}H_{12}O_2$ requires C, 73.15; H, 7.4%; *M*, 164.083 7); $\lambda_{max.}$ 237(sh), 272.5 nm (log ε 3.49, 4.15); $\nu_{max.}$ 1 660 cm^{-1}, δ 1.33 (6 H, s, Me_2), 2.10 (2 H, t, *J* 6 Hz, CH_2), 2.65 (2 H, t, *J* 6 Hz, CH_2), 6.5 (1 H, d, *J* 2 Hz, Ar-H), and 7.63 (1 H, d, *J* 2 Hz, Ar-H).

(*iv*) 4-Methyl-1-(3-pyridyl)pentylideneamino-oxyacetic acid, like the other pyridine acids, was soluble in water and no alkali was added before addition of persulphate. It gave after chromatography of the product mixture, using ethyl acetate–methylene chloride (1 : 1) as eluant (*a*) 8,8-*dimethyl*-5,6,7,8-*tetrahydroquinolin*-5-*one* (25%), m.p. 54—56 °C (sublimation) (Found: M^+, 175.099 7. $C_{13}H_{13}NO$ requires *M*, 175.099 7); $\lambda_{max.}$ 208.5, 233, and 277 nm (log ε 4.03, 3.92, and 3.62); $\nu_{max.}$ 1 690 cm^{-1}; δ 1.43 (6 H, s, Me_2), 2.05 (2 H, t, *J* 7 Hz, CH_2), 2.75 (2 H, t, *J* 7 Hz, CH_2), and 7.25, 8.25, 8.75 (each 1 H, m, Ar-H); its 2,4-*dinitrophenylhydrazone* had m.p. 248.5—251 °C (ethanol) (Found: M^+, 355.128 1. $C_{17}H_{17}N_5O_4$ requires *M*, 355.128 0): (*b*) 5,5-*dimethyl*-5,6,7,8-*tetrahydroisoquinolin*-8-*one* (21%), m.p. 128—131 °C (sublimation) (Found: C, 75.2; H, 7.8; N, 8.1%; M^+, 175.099 7. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.5; N, 8.0%. *M*, 175.0997); $\lambda_{max.}$ 209, 237.5, 267sh, 276sh, and 305 nm (log ε 4.15 3.93 3.33 3.23 and 2.86); $\nu_{max.}$ 1 680 cm^{-1}; δ 1.4 (6 H, s, Me_2), 2.05 (2 H, t, *J* 7 Hz, CH_2), 2.75 (2 H, t, *J* 7 Hz, CH_2), 7.2 (1 H, d, *J* 6 Hz, 4-Ar-H), 7.6 (1 H, d, *J* 6 Hz, 3-Ar-H), and 9.05 (1 H, s, 1-ArH); its 2,4-*dinitrophenylhydrazone* had m.p. 149—153.5 °C (from methanol) (Found: M^+, 355.128 1. $C_{17}H_{17}N_5O_4$ requires *M*, 355.128 0).

(*v*) 1-(3-Pyridyl)pentylideneamino-oxyacetic acid gave, after chromatography as in (*iv*); (*a*) 8-*methyl*-5,6,7,8-*tetrahydroquinolin*-5-*one* (18%) as an oil [b.p. *ca.* 160 °C (Kugel)/1.0 mmHg] (Found: M^+, 161.084 3. $C_{10}H_{11}NO$ requires *M*, 161.084 1); $\nu_{max.}$ 1 695 cm^{-1}; δ 1.47 (3 H, d, *J* 7 Hz, Me), 1.5—2.9 (5 H, m, CH_2CH_2CH), 7.3 (1 H, dd, *J* 8 and 4 Hz, 3-Ar-H), 8.25 (1 H, dd, 8 and 2 Hz, 4-Ar-H), 8.7 (1 H, dd, *J* 4 and 2 Hz, 2-ArH); its 2,4-*dinitrophenylhydrazone* had m.p. 227—230 °C (from methanol) (Found: M^+, 341.112 2. $C_{16}H_{15}N_5O_4$ requires *M*, 341.112 4); (*b*) 5-*methyl*-5,6,7,8-*tetrahydroisoquinolin*-8-*one* (12%) as an oil (b.p. 156—160 °C/0.65 mmHg) (Found: M^+, 161.084 0. $C_{10}H_{11}NO$ requires *M*, 161.084 1); $\nu_{max.}$ 1 695 cm^{-1}; δ 1.45 (3 H, d, *J* 5 Hz, Me), 1.5—3.3 (5 H, m, CH_2CH_2CH), 7.3 (1 H, d, *J* 4 Hz, 4-Ar-H), 8.65 (1 H, d, *J* 4 Hz, 3-Ar-H), and 9.1 (1 H, s, 1-Ar-H); its 2,4-*dinitrophenylhydrazone* had m.p. 218—220 °C (from methanol) (Found: M^+, 341.112 2. $C_{15}H_{15}N_5O_4$ requires *M*, 341.112 4).

(vi) 1-(4-Pyridyl)pentylideneamino-oxyacetic acid gave 8-*methyl*-5,6,7,8-*tetrahydroisoquinolin*-5-*one* as an oil (Found: M^+, 161.084 1. $C_{10}H_{11}NO$ requires *M*, 161.084 1); $\nu_{max.}$ 1 695 cm^{-1}; δ 1.4 (3 H, d, *J* 6 Hz, Me), 1.5—2.9 (5 H, m, $CHCH_2CH_2$), 7.85 (1 H, m, 3-Ar-H), 8.5 (1 H, m, 1-Ar-H), 8.7 (1 H, m, 4-Ar-H); its 2,4-*dinitrophenylhydrazone* had m.p. 117—121 °C (from methanol) (Found: M^+, 341.112 2. $C_{16}H_{15}N_5O_4$ requires *M*, 341.112 4).

Preparation and Photolysis of Bis-[4-*methyl*-1-(2-*thienyl*)-*pentylideneamino*]-*oxalate*.—A solution of oxalyl chloride (0.005 mol) in ether (10 ml) was added dropwise to a stirred solution of 4-methyl-1-(2-thienyl)pentan-1-one oxime (0.011 mol) in ether at 0 °C under nitrogen. The reaction mixture was stirred for 5 h and left overnight at 0 °C. The solution was concentrated and the solid which separated was collected. Crystallisation from ether gave the *product* (50%), m.p. 98—100 °C (Found: C, 58.6; H, 6.2; N, 5.9; S,

* This was contaminated with sodium sulphate and a reliable m.p. could not be obtained.

† This was contaminated with sodium chloride.

14.0%; M^+, 448.146 8. $C_{22}H_{28}N_2O_4$ requires C, 58.9; H, 6.3; N, 6.25; S, 14.3%; M, 448.146 8); $\nu_{max.}$ 1 760 and 1 790 cm^{-1}; δ 1.0 (6 H, d, J 5 Hz, Me_2), 1.6 (3 H, m, CH_2-CH), 2.9 (2 H, br t, J 8 Hz, CH_2), and 7.0—7.5 (3 H, m, Ar-H).

The oxalate (0.001 mol) in benzene (75 ml) and trifluoroacetic acid (1.5 ml) was photolysed using a 500-W medium-pressure Hanovia lamp in a ' falling curtain reactor ' for 10 min. The solution was then concentrated and chromatographed using chloroform as eluant to give 4,4-dimethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophen-7-one (15%), identical with that produced in (*i*). The starting oxalate and the parent ketone were also present but were not isolated. The photolysis was repeated: (*a*) without addition of trifluoroacetic acid, only the oxalate and the parent ketone were present (t.l.c.); and (*b*) with trifluoroacetic acid (5 ml) there was no increase in the yield of cyclic ketone.

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