

Synthesis of aminoquinolones from triazoles *via* carboxamido-ketenimine and amidinoketene intermediates

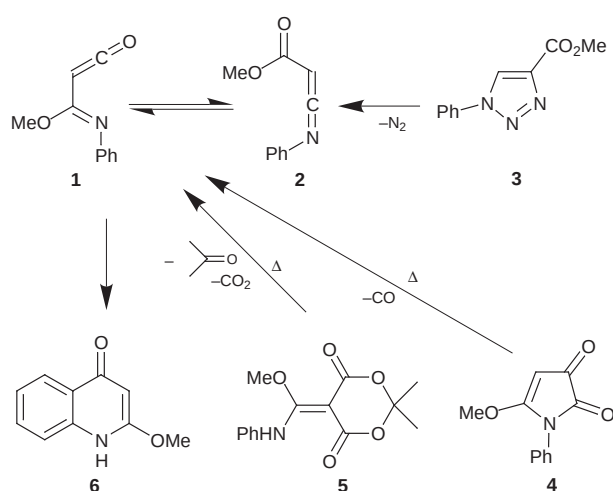
V. V. Ramana Rao and Curt Wentrup*

Department of Chemistry, The University of Queensland, Brisbane, Qld 4072, Australia

1-Aryl-1*H*-1,2,3-triazole-4-carboxamides **7d–f** have been synthesized and converted to 2-dimethyl-amino-4-quinolones **12d–f** by flash vacuum thermolysis (FVT). The reaction takes place *via* carboxamidoketenimine **9** and amidinoketene intermediates **10**. The former are observed by FTIR spectroscopy at 77 K or in Ar matrices at 12 K.

Introduction

It has been shown in previous work that imidoalkenes **1** and α -oxoketenimines **2** undergo thermal interconversion *via* 1,3-migration of alkoxy groups, resulting in the synthetically useful formation of 2-methoxyquinolones (**6**). Triazoles (**3**),^{1,2} pyrrole-2,3-diones (**4**)³ and Meldrum's acid precursors (**5**),² can all be

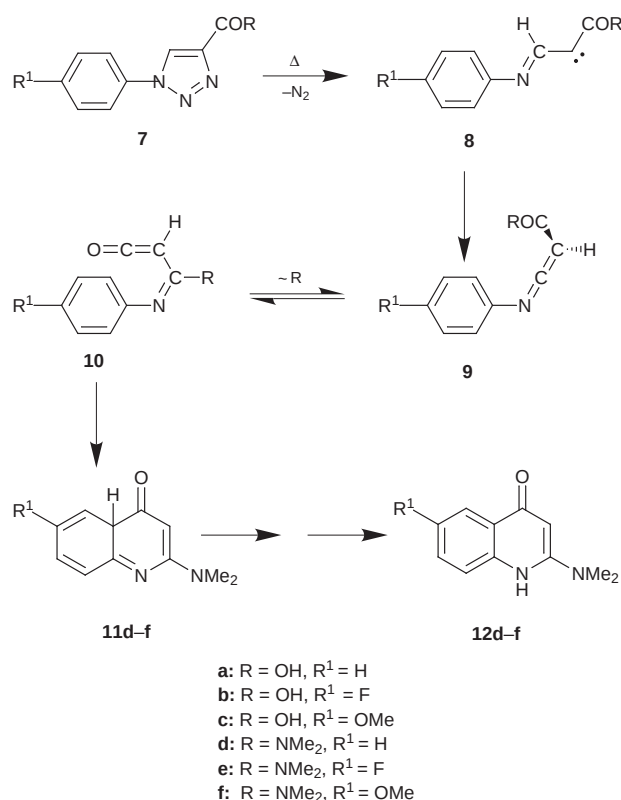


employed. In the case of triazoles, indoles may be formed as by-products.² 2-(Alkylthio)quinolones are obtained analogously.^{4a} The migratory aptitudes of methoxy and other groups in the interconversion of **1** and **2** have been investigated both experimentally and theoretically, and very facile migration of electron donating groups, especially those possessing lone pairs, are to be expected ($R = R'O, R'S, R'_2N$, halogens).⁴

Because of widespread interest in quinolones (especially 6-fluoro-4-quinolones) as *inter alia* potential antibiotics⁵ and anti-cancer compounds,⁶ we have investigated the use of the triazole methodology to prepare previously little-known 2-dimethylamino-4-quinolone derivatives and report the results herein. Only a few differently substituted 2-aminoquinolones have been prepared in other ways.^{4e,7}

Results and discussion

The triazolecarboxamides **7d–f** were prepared from the carboxylic acids **7a–c**, themselves obtained from the corresponding ethyl esters (Scheme 1). Structural assignments of the compounds were made on analytical and spectroscopic grounds. The vinylic hydrogen atoms 5-H appear as sharp singlets in the region of 8.5 ppm in the ¹H NMR spectra. The ¹³C NMR spectrum of **7d** displays signals at δ 125.9, 145.0 and 160.9 ppm assigned to 5-C, 4-C and C=O, respectively, on the basis of chemical shifts and the results of DEPT experiments.



Scheme 1

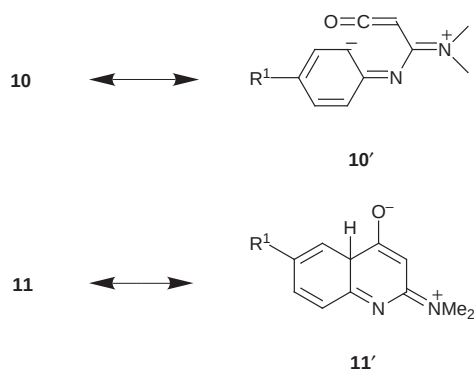
The 6-fluoro derivative **7e** exhibits doublets due to carbon-fluorine couplings in the ¹³C NMR spectrum. The doublet at δ 116.7 ppm was assigned to the 3'-C ($J_{CF} = 23$ Hz), a doublet at δ 122.5 ppm to 2'-C ($J_{CF} = 8.6$ Hz), and a doublet at 162.5 ppm to 4'-C ($J_{CF} = 248$ Hz), on the basis of chemical shifts, coupling constants, and a DEPT experiment.

Preparative flash vacuum thermolysis (FVT) of triazolecarboxamide **7d** at 600 °C with isolation of the product on a liquid N₂ cooled cold finger resulted in the formation of quinolone **12d** in 69% isolated yield. Preparative FVT of **7e** and **7f** at 600 °C similarly yielded the quinolones **12e** (63%) and **12f** (57%), respectively. In the ¹H NMR spectrum of **12d** the one-proton signal at δ 5.44 ppm (broad singlet) was assigned to the vinylic 3-H, and another broad one-proton signal at δ 10.20 ppm to N-H. This was confirmed by deuterium exchange with D₂O, which caused rapid exchange of the N-H proton, whereas 3-H exchanged slowly in the course of 24 h. This phenomenon is characteristic of all the 2-aminoquinolin-4-ones and presumably is due to intervention of the 3*H* tautomer.

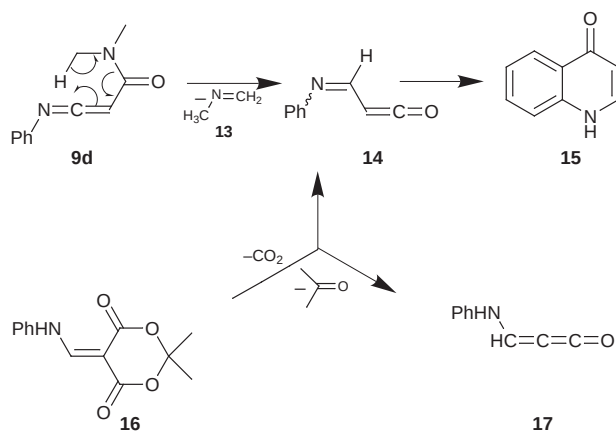
In the ¹³C NMR spectrum of **12d**, three signals at δ 89.9, 154.4 and 168.4 ppm were assigned to 3-C, 2-C and C=O,

respectively, and the signals at δ 118.4, 122.7, 123.3, 125.3, 131.4 and 139.7 ppm to aromatic carbons on the basis of comparison with analogous compounds.² These assignments were confirmed by a HMQC direct ^1H – ^{13}C correlation, which linked the ^1H NMR signals with the secondary carbon atoms at 131.4, 125.3, 123.3, 122.7 and 89.9 ppm. The structures of quinolones **12e** and **12f** were assigned in a similar manner.

In order to observe the postulated ketenimine intermediates **9** directly, the products of FVT of amide **7d** were isolated at either 77 K (neat, on BaF_2) or 12 K (Ar matrix, on KBr) for FTIR spectroscopy. At an FVT temperature of 400 °C, only starting material was observed. At 500 °C, a medium signal assigned to the ketenimine **9d** [2041/2032 cm^{-1} neat; 2051/2032 cm^{-1} (with several minor bands) in Ar matrix] appeared. A very weak ketene signal at 2129 cm^{-1} (neat) was also observed (see below). The occurrence of double signals for the ketenimines (e.g. 2041/2032 cm^{-1}) is consistent with previous observations.^{2,4d,8} At higher FVT temperatures (700–800 °C), the ketenimine signals diminished, disappearing completely above 800 °C. As the ketenimine signals decreased in intensity, those due to the final product, quinolone **12d**, increased. However, other decomposition products also appeared in the IR spectra above 500 °C, increasing in intensity up to at least 800 °C, including *N*-methylmethanimine **13**, phenyl isocyanate, and *N*-phenyliminopropadienone ($\text{PhN}=\text{C}=\text{C}=\text{O}$), identified by their characteristic IR bands,⁹ as well as unidentified absorptions at 2128, 2138 (possibly CO) and 2142 cm^{-1} (Ar matrix). Control experiments showed that these bands are not due to the C-unsubstituted *N*-phenylimidoylketene **14** (see below).¹⁰ The fact that these absorptions persist at high temperatures excludes the possibility that they could be due to ketene **10d**. It is questionable whether this first-formed ketene **10d** was observed at all: the very weak ketene bands recorded under mild FVT conditions (500 °C) could be due to traces of the above mentioned decomposition products. At any rate, ketenes **10** are very difficult to observe, giving at best only very weak absorptions, whereas the ketenimines **9** are more easily observed, in agreement with earlier results for other ketenes and ketenimines.² The difficulty of observing **10** is also in agreement with the finding in other research that the cyclization of amidinoketenes to quinolones is extremely facile, taking place at or below room temperature.^{4e,11} This can be ascribed to activation of the aromatic ring in **10** (see resonance structure **10'**) as well as stabilization of the 4a*H*-quinoline intermediate (**11** $\longleftrightarrow$ **11'**) by the NMe_2 group. Therefore, the stationary concentration of **10** under FVT conditions can be expected to be very low.



Preparative FVT experiments demonstrated that quinolone **12d** is still the major product at 800 °C (54% yield), but small amounts of the unsubstituted quinolone **15** appeared as well ($\leq 10\%$). Control experiments showed that **12d** is completely stable to FVT at 600 °C, but at 800 °C it underwent partial decomposition to **15** ($\leq 10\%$). Although there is always the possibility of chemical activation in FVT reactions at low pressure,¹² resulting in vibrationally hot **12d** which therefore undergoes partial elimination of *N*-methylmethanimine **13** already at 500–600 °C, another likely route to quinolone **15** needs to be



Scheme 2

considered (Scheme 2). A retro-ene reaction of ketenimine **9d** would provide **13** and imidoylketene **14**, the latter cyclizing to **15**. We have recently reported a variety of retro-ene reactions taking place in other ketene and acylallene derivatives.^{4c,9a} For comparison, imidoylketene **14** was also generated by FVT of the Meldrum's acid derivative **16**. In conformity with earlier research,¹⁰ in which ketenes **14** and **17** were isolated neat at -196 °C for IR spectroscopy, Ar matrix isolation of the products of FVT of **16** at 500–600 °C revealed two ketenes absorbing at 2099 and 2131 cm^{-1} (**17** and **14**, respectively). Both of these products disappeared on FVT at 700 °C. Preparative FVT of **16** above 450 °C gave quinolone **15**. Just like imidoylketenes **10**, any imidoylketene **14** formed in a retro-ene reaction of **9d** would be difficult to detect due to the facile cyclization to **15**.

Analogous experiments with low temperature isolation of the products of FVT of triazoles **7e** and **7f** at 450–470 °C gave rise to ketenimine signals for **9e** (2041 cm^{-1} neat; 2045 cm^{-1} in Ar matrix) and **9f** (2026 cm^{-1} neat; 2035 cm^{-1} in Ar) (several bands in each case; only the maximum is given). Here, too, the corresponding ketenes **10e,f** were difficult to observe or absent, and IR bands due to *N*-methylmethanimine and other decomposition products appeared and grew at FVT temperatures above ca. 500 °C.

In all cases, the desired 2-(dimethylamino)quinolones **12** are easily separated from any potential decomposition products due to their great insolubility in most common solvents. Thus, simple washing of the FVT products with acetone removes all impurities, leaving essentially pure quinolone **12**.

Conclusions

FVT of 1-aryl-1,2,3-triazole-4-carboxamides **7** is a convenient means of preparation of 2-amino-4-quinolones (**12**) in yields of 60–70%. 6-Substituted quinolones are obtained selectively from the 1-(*p*-substituted aryl)triazoles, themselves prepared from *p*-substituted anilines. These reactions take place *via* observable intermediate carboxamidoketenimines (**9**), which are not, however, isolable at room temperature. Interconversion between **9** and amidinoketenes **10** *via* a 1,3-shift of the dimethylamino group is calculated to have a very low activation barrier, of the order of 26 kJ mol^{-1} .^{4b,f,g} The amidinoketenes **10** so formed undergo facile electrocyclization to quinolones (**12**). On FVT of **7** at higher temperatures (>500 °C), competing fragmentation reactions lead to *N*-methylmethanimine and other products. However, these competing reactions do not significantly hamper the preparation of quinolones **12**.

Experimental

The FVT apparatus and general equipment were as previously reported for Ar matrix (12 K),¹³ 77 K deposition,¹⁰ and preparative scale work (77 K isolation).¹⁴ Melting points are uncor-

rected. NMR spectra were recorded at 200 MHz for ^1H and 50 MHz for ^{13}C . All J values are given in Hz. Triazole esters **7** ($\text{R} = \text{OEt}$) were prepared from ethyl propiolate and aryl azides, themselves prepared from the corresponding anilines, according to literature procedures.¹⁵ Azides are potentially explosive, and due care should be exercised working with them. 2,2-Dimethyl-5-(phenylaminomethylene)-1,3-dioxane-4,6-dione **16** and quinolone **15** were prepared as previously described.^{10,16}

General procedure for the preparation of 1-aryl-1*H*-1,2,3-triazole-4-carboxylic acids **7a–c**

A mixture of the corresponding triazole ethyl ester¹⁵ (10 mmol) and 6 M HCl (20 cm³) was stirred at 80 °C overnight. The mixture was cooled to 10 °C and the solid was filtered, washed with water and dried. GCMS analysis of the crude materials indicated that the acids **7a–c** had been formed in good purity; **7a**: off-white solid; crude yield 75%; **7b**: white crystals; crude yield 82%; **7c**: pale brown light solid; crude yield 68%. The carboxylic acids were used without further purification in the next step.

Representative procedure for the preparation of *N,N*-dimethyl-1-aryl-1*H*-1,2,3-triazole-4-carboxamides **7d–f**

Compound **7a** (0.9 g, 4.76 mmol) in SOCl_2 (10 cm³) was refluxed for 1 h under N_2 . Excess SOCl_2 was removed by distillation with protection from moisture. Dimethylamine (2 equiv.) in CH_2Cl_2 was added dropwise to a cold (10 °C) solution of the crude acid chloride in CH_2Cl_2 (10 cm³). After the mixture had been stirred for 30 min, it was washed with water (2 × 25 cm³). The organic layer was washed with saturated aq. NaCl, dried (Na_2SO_4), and concentrated to furnish a white solid (1 g). The crude product was recrystallized in hot CCl_4 (10 cm³) to give *N,N*-dimethyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxamide **7d** (0.9 g, 87%), mp 150–151 °C (Found: C, 60.74; H, 5.58; N, 26.15; M^+ 216.1014. $\text{C}_{11}\text{H}_{12}\text{N}_4\text{O}$ requires C, 61.08; H, 5.60; N, 25.92%; M^+ 216.1011); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3115, 1623, 1614, 1545, 1394, 1249, 1158, 1046, 865, 766; $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$ 3.16 (3H, s, CH_3), 3.60 (3H, s, CH_3), 7.47–7.60 (3H, m, ArH), 7.75–7.80 (2H, m, ArH), 8.56 (1H, s, 5-H); $\delta_{\text{C}}(50 \text{ MHz}; \text{CDCl}_3)$ 36.2 (CH_3), 38.6 (CH_3), 120.4, 125.9 (CH, C-5), 129.0, 129.8, 136.3, 145.0 (quat., C-4), 160.9 (C=O).

N,N-Dimethyl-1-(*p*-fluorophenyl)-1*H*-1,2,3-triazole-4-carboxamide **7e**. Prepared from 0.8 g of **7b** to give 0.77 g (85%) after crystallization from CCl_4 –EtOH (4:1), mp 183–185 °C (Found: C, 56.35; H, 4.84; N, 23.83; M^+ 234.0917. $\text{C}_{11}\text{H}_{11}\text{N}_4\text{OF}$ requires C, 56.39; H, 4.74; N, 23.93%; M^+ 234.0917); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3112, 1616, 1542, 1518, 1385, 1258, 1161, 1039, 845, 766; $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$ 3.16 (3H, s, CH_3), 3.60 (3H, s, CH_3), 7.24 (2H, dd, J 7.9 and 10.1), 7.78 (2H, dd, J 4.6 and 9.1), 8.58 (1H, s, 5-H); $\delta_{\text{C}}(\text{CDCl}_3)$ 36.2 (CH_3), 38.6 (CH_3), 116.7 (C-3', d, J_{CF} 23), 122.5 (C-2', d, J_{CF} 8.6), 126.2 (CH, C-5), 132.7 (quat., C-1'), 145.2 (quat., C-4), 160.8 (C=O), 162.5 (C-4', d, J_{CF} 248).

N,N-Dimethyl-1-(*p*-methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxamide **7f**. Prepared from 0.95 g of **7c** to give 0.7 g (65%), mp 145–147 °C (Found: C, 58.38; H, 5.71; N, 22.54; M^+ 246.1117. $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_2$ requires C, 58.51; H, 5.73; N, 22.76%; M^+ 246.1117); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3132, 1636, 1538, 1525, 1393, 1258, 1178, 1043, 826, 759; $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$ 3.16 (3H, s, CH_3), 3.60 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 7.04 (2H, d, J 9.0), 7.66 (2H, d, J 9.0), 8.43 (1H, s, 5-H); $\delta_{\text{C}}(\text{CDCl}_3)$ 36.4 (CH_3), 38.8 (CH_3), 55.6 (OCH_3), 114.9, 122.2, 126.0, 129.9, 145.0 (quat., C-4), 160.1 (quat., OCH_3), 161.2 (C=O).

General procedure for the synthesis of quinolones **12d–f** (FVT of **7d–f**)

Compounds **7d–f** were vaporized at 80–130 °C (depending on volatility) into the preparative thermolysis tube maintained at 600 °C in the course of 4 h. The thermolysate was condensed on the cold finger at 77 K (liq. N_2). Upon completion of the reaction, the system pressure was equalized with N_2 , and the product was collected after rinsing the cold finger with acetone

(which dissolves any impurities), and recrystallized from CHCl_3 –MeOH (3:1).

2-(*N,N*-Dimethylamino)-4-quinolone (12d). Cream solid; yield 69% (at 800 °C the same compound was obtained in 54% yield); mp 294–296 °C (decomp.) (Found: C, 69.88; H, 6.42; N, 14.53; M^+ 188.0950. $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$ requires C, 70.18; H, 6.43; N, 14.89%; M^+ 188.0950); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3438, 1641, 1594, 1541, 1490, 1466, 1435, 1402, 1346, 1301, 1262, 1170, 801, 752; $\delta_{\text{H}}(200 \text{ MHz}; [\text{D}_6]\text{DMSO})$ 3.07 (6H, s, 2 × CH_3), 5.44 (1H, br s, 3-H), 7.13 (1H, t, J 7.3), 7.46 (1H, t, J 7.0 and 7.3), 7.55 (1H, d, J 7.9), 7.90 (1H, d, J 7.9), 10.20 (1H, br s, NH); $\delta_{\text{C}}([\text{D}_6]\text{DMSO})$ 39.2 [$\text{N}(\text{CH}_3)_2$], 89.9 (CH, C-3), 118.4, 122.7, 123.3, 125.3, 131.4, 139.7, 154.4 (quat., C-2), 168.4 (C=O).

2-(*N,N*-Dimethylamino)-6-fluoro-4-quinolone (12e). Cream solid; yield 63%; mp 297–299 °C (decomp.) (Found: C, 63.91; H, 5.42; N, 13.22; M^+ 206.0855. $\text{C}_{11}\text{H}_{11}\text{N}_2\text{OF}$ requires C, 64.05; H, 5.38; N, 13.59%; M^+ 206.0855); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3440, 1635, 1602, 1544, 1469, 1423, 1399, 1553, 1299, 1255, 1195, 1170, 946, 819, 805, 730; $\delta_{\text{H}}(200 \text{ MHz}; [\text{D}_6]\text{DMSO})$ 3.06 (6H, s, 2 × CH_3), 5.70 (1H, br s, 3-H), 7.28 (1H, dt, J 3.5 and 8.7), 7.55 (1H, dd, J 3.1 and 9.5), 7.61 (1H, dd, J 4.8 and 9.1), 10.26 (1H, br s, NH); $\delta_{\text{C}}([\text{D}_6]\text{DMSO})$ 38.9 [$\text{N}(\text{CH}_3)_2$], 89.9 (CH, C-3), 107.7, 108.8, 118.3, 119.0, 135.5, 154.1 (quat., C-2), 156.3 (quat., C-6), 173.8 (C=O).

2-(*N,N*-Dimethylamino)-6-methoxy-4-quinolone (12f). Cream solid; yield 57%; mp 264–266 °C (decomp.) (Found: M^+ 218.1053. $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$ requires M^+ 218.1055); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3429, 1646, 1602, 1535, 1461, 1401, 1297, 1172, 828; $\delta_{\text{H}}(200 \text{ MHz}; [\text{D}_6]\text{DMSO})$ 3.03 (6H, s, 2 × CH_3), 3.76 (3H, s, OCH_3), 5.47 (1H, br s, 3-H), 7.00 (1H, dd, J 2.6 and 8.8), 7.30 (1H, d, J 2.6), 7.65 (1H, d, J 8), 10.49 (1H, br s, N-H); $\delta_{\text{C}}([\text{D}_6]\text{DMSO})$ 38.8 [$\text{N}(\text{CH}_3)_2$], 55.2 (OCH_3), 89.3 (CH, C-3), 107.2, 119.7, 120.2, 122.5, 133.9, 152.4 (quat., C-2), 154.3 (quat., C-6), 171.5 (C=O).

FVT/matrix isolation

The triazoles **7** (30 mg) were placed in the quartz thermolysis tube in an oven directly attached to the vacuum system. After evacuating the oven, the cryostat was turned on and the pressure brought to 2×10^{-5} mbar while the BaF_2 disk reached a temperature of 12 K. Argon was passed over the sample while it was sublimed at ca. 80 °C through the FVT tube maintained at different temperatures, and the products were co-deposited on the disk at 12 K for FTIR spectroscopy. Deposition at 77 K was performed analogously, except that no carrier gas was used, and the deposition disk was cooled with liquid N_2 .

FVT of 16. Carried out as previously described¹⁰ with isolation of the products neat at –196 °C or in Ar matrix at 12 K for IR spectroscopy. Preparative FVT of **16** at 500 and 600 °C gave pure quinolone **15**.^{10,16}

High temperature FVT of 7d. The formation of small amounts ($\leq 10\%$) of **15** on FVT of **7d** above 600 °C was established by TLC and ^1H NMR spectroscopy of the acetone-soluble portion of the thermolysate (recorded in CDCl_3 solution) with direct comparison with the authentic material. The acetone-insoluble fraction under these conditions was pure quinolone **12d** (NMR recorded in $[\text{D}_6]\text{DMSO}$).

Acknowledgements

This research was supported by the Australian Research Council. We thank Dr Jens Morawietz for initial assistance with matrix isolation experiments.

References

- 1 D. Clarke, R. W. Mares and H. McNab, *J. Chem. Soc., Chem. Commun.*, 1993, 1020; *J. Chem. Soc., Perkin Trans. 1*, 1997, 1799.
- 2 B. E. Fulloon and C. Wentrup, *J. Org. Chem.*, 1996, **61**, 1363.

- 3 B. E. Fulloon, H. A. A. El-Nabi, G. Kollenz and C. Wentrup, *Tetrahedron Lett.*, 1995, **36**, 6547.
- 4 (a) C. O. Kappe, G. Kollenz, R. Leung-Toung and C. Wentrup, *J. Chem. Soc., Chem. Commun.*, 1992, 487; (b) M. W. Wong and C. Wentrup, *J. Org. Chem.*, 1994, **59**, 5279; (c) D. W. J. Moloney, M. W. Wong, R. Flammang and C. Wentrup, *J. Org. Chem.*, 1997, **62**, 4240; (d) V. V. R. Rao, B. E. Fulloon, P. V. Bernhardt, R. Koch and C. Wentrup, *J. Org. Chem.*, 1998, **63**, in the press; (e) C. Wentrup, B. E. Fulloon, D. W. J. Moloney, H. Bibas and M. W. Wong, *Pure Appl. Chem.*, 1996, **68**, 891; (f) J. Finnerty, J. Andraos, Y. Yamamoto, M. W. Wong and C. Wentrup, *J. Am. Chem. Soc.*, 1998, **120**, 1701; (g) M. W. Wong and C. Wentrup, unpublished calculations.
- 5 D. Niccolai, L. Tarsi and R. J. Thomas, *Chem. Commun.*, 1997, 2333; K. Grohe, *Chem. Brit.*, 1992, 34; Y. Asahina, T. Ishizaki and S. Suzue, in *Progress in Drug Research*, ed. S. Mitsuhashi, Birkhauser, Basel, 1992, vol. 38, pp. 57–106.
- 6 S.-C. Kuo, H.-Z. Lee, J.-P. Juang, Y.-T. Lin, T.-S. Wu, J.-J. Chang, D. Lednicer, K. D. Paull, C. M. Lin, E. Hamel and K.-H. Lee, *J. Med. Chem.*, 1993, **36**, 1146.
- 7 G. Himbert, in *Houben-Weyl: Methoden der Organischen Chemie*; Thieme Verlag, Stuttgart, 1993, vol. E 15/3, p. 3426, and references therein. M. E. Kuehne and P. J. Sheehan, *J. Org. Chem.*, 1968, **33**, 4406; K. T. Potts, R. Ehlinger and W. M. Nichols, *J. Org. Chem.*, 1975, **40**, 2596.
- 8 (a) *N*-Phenylketenimine absorbs in N₂ matrix at 2050, 2030 cm⁻¹.^{8b} In Ar matrix it absorbs at 2048, 2032 cm⁻¹.^{8c} and in CCl₄ solution at room temperature at 2040, 2020 cm⁻¹ (both absorptions are very strong).^{8d} (b) E. Orton, S. T. Collins and G. C. Pimentel, *J. Phys. Chem.*, 1986, **90**, 6139; (c) B. Freiermuth and C. Wentrup, previously unpublished measurements; (d) H.-W. Winter and C. Wentrup, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 720.
- 9 (a) *N*-Methylmethanimine: H. Bibas, R. Koch and C. Wentrup, *J. Org. Chem.*, 1998, **63**, 2619; (b) *N*-Phenyliminopropadienone: T. Mosandl, S. Stadtmüller, M. W. Wong and C. Wentrup, *J. Phys. Chem.*, 1994, **98**, 1080; (c) Phenyl isocyanate: C. O. Kappe, G. Kollenz and C. Wentrup, *Acta Chem. Scand.*, 1993, **47**, 940.
- 10 H. Briehl, A. Lukosch and C. Wentrup, *J. Org. Chem.*, 1984, **49**, 2772.
- 11 D. J. W. Moloney, PhD Thesis, The University of Queensland, 1997; A. Bouvy, Z. Janousek, H. G. Viehe and J. M. Arietta, *Bull. Soc. Chim. Belg.*, 1985, **94**, 869.
- 12 C. Wentrup, *Reactive Molecules*, Wiley, New York, 1984, p. 225.
- 13 C. O. Kappe, M. W. Wong and C. Wentrup, *J. Org. Chem.*, 1995, **60**, 1686–1695.
- 14 C. Wentrup, R. Blanch, H. Briehl and G. Gross, *J. Am. Chem. Soc.*, 1988, **110**, 1874.
- 15 S. T. Abu-Orabi, M. A. Atfah, I. Jibril, F. M. Mari'i and A. A. Ali, *J. Heterocycl. Chem.*, 1989, **26**, 1461; R. Huisgen, R. Knorr, L. Möbius and G. Szeimies, *Chem. Ber.*, 1965, **98**, 4014.
- 16 I. Hermecz, G. Kereszturi and L. Vasvari-Debreczy, *Adv. Heterocycl. Chem.*, 1992, **54**, 252 and references therein.

Paper 8/02768D

Received 14th April 1998

Accepted 11th June 1998