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UNUSUAL SUBSTITUENT MIGRATION IN 4-ALLYLOXY-3-(2-BENZYLBENZOYL)-2-METHYLQUINOLINES

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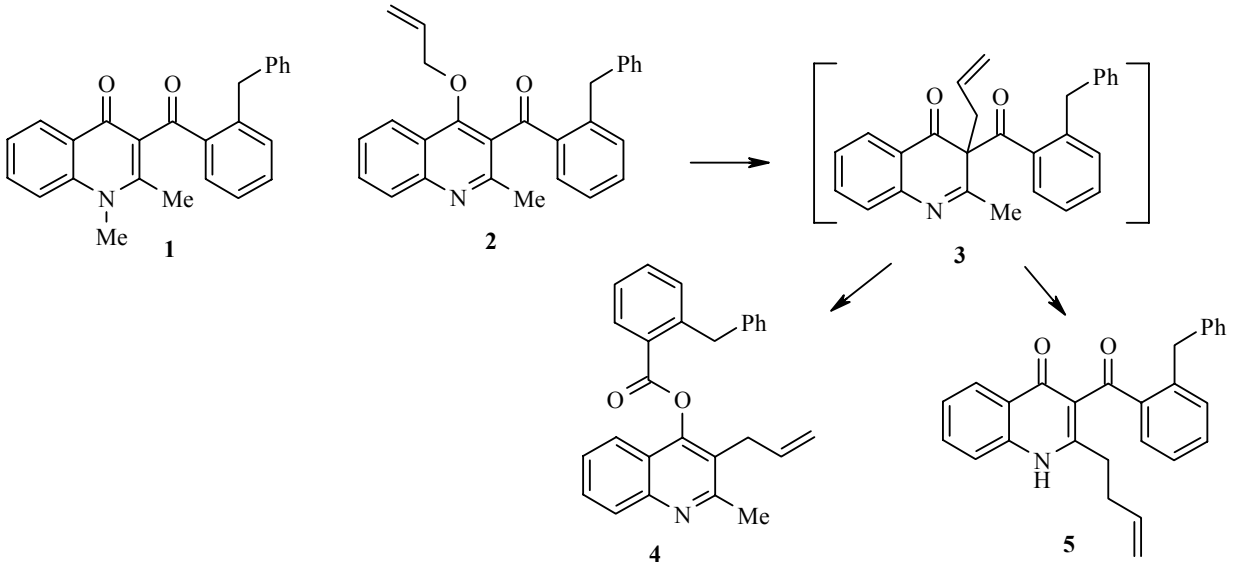
Photoreversible photochromic systems have received considerable attention in light of their potential as components in optoelectronic devices [1]. In previous work [2], we showed that colorless 3-(2-benzylbenzoyl)-1,2-dimethyl-4(1H)quinolone (**1**) undergoes a reversible photoinduced cyclization to give a red fluorescent product. We have subsequently studied such quinolones with substituents at C-2, which are capable of undergoing polymerization.



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Ketone **2**, which was obtained in 60% yield from the corresponding N-unsubstituted quinolone and allyl bromide in DMF/K_2CO_3, appeared to be a promising precursor for such purposes. We might have expected that ketone **2** would undergo a series of Claisen and Cope rearrangements already described for 3-methyl- [3] and 3-ethoxycarbonyl-substituted [4] 4-allyloxyquinolones to give the desired 2-(4-butenyl)quinolone **5**. However, heating ketone **2** in *o*-dichlorobenzene at reflux unexpectedly gave (3-allyl-2-methyl-4-quinolinyl)-2-benzyl benzoate **4** in 48% yield as the major product. It would be logical to assume that benzoate **4** would be formed from Claisen rearrangement intermediate **3**. Indeed, a similar benzoyl group migration was recently postulated to explain the composition of the reaction products upon vacuum flash thermolysis at 650°C [5]. In our case, the 1,3-shift of the 2-benzylbenzoyl group from carbon to oxygen occurs at relatively low temperature and competes efficiently with the Cope rearrangement step. The direction of the reaction can probably be attributed to steric hindrance by the bulky 2-benzylbenzoyl group. Indeed, substituent exchange at C-2 and C-3 is not observed for the 3-benzoyl analog and the expected 3-benzoyl-2-butenylquinolone was obtained under the same conditions as the only product.

In light of the special importance of 4-quinolones as biologically active compounds [6], the systematic study of this unexpected sequence of rearrangements may open new synthetic approaches to previously unknown 3-substituted 4-quinolone derivatives that have been difficult to obtain.

The ^{1}H and ^{13}C NMR spectra were taken on a Bruker 250 spectrometer at 250 and 65 MHz, respectively, in DMSO-d_6 (compound **4**) and $CDCl_3$ (for compound **5**) with TMS as the internal standard.

Preparation of (2-Methyl-3-prop-2-en-1-ylquinolin-4-yl)-2-benzylbenzoate (4) and 3-[(2-Benzyl-phenyl)-carbonyl]-2-but-3-en-1-ylquinolin-4(1H)-one (5). A solution of ketone **2** (690 mg) in *o*-dichloro-benzene (10 ml) was heated at reflux for 1 h. Separation on a silica gel column using ethyl acetate–cyclohexane as the eluent gave 210 mg (30%) quinolone **5** as a colorless powder, mp 186-187°C and 330 mg (48%) benzoate **4** as colorless crystals, mp 125-126°C (heptane).

Benzoate 4. ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (a) benzoyl, b) benzyl, d) allyl groups): 2.76 (3H, s, CH_3); 3.34-3.46 (2H, m, 1d-CH_2), 4.51 (2H, s, C$\underline{H}_2$Ph); 4.94 (1H, dtd, *J* = 17.1, *J* = 1.7, *J* = 1.5, H-3d *trans*); 5.04 (1H, dtd, *J* = 10.2, *J* = 1.6, *J* = 1.5, H-3d *cis*); 5.83 (1H, ddt, *J* = 17.1, *J* = 10.2, *J* = 5.8, H-2d); 7.10-7.20 (2H, m, H-3b and H-5b); 7.20-7.31 (3H, m, H-2b, H-4b, H-6b); 7.32-7.52 (4H, m, H-3a, H-5a, H-4a, H-7); 7.59-7.67 (1H, m, H-6a); 7.65 (1H, ddd, *J* = 8.5, *J* = 6.6, *J* = 1.8, H-6); 8.03 (1H, ddd, *J* = 8.5, *J* = 0.8, *J* = 0.7, H-5); 8.3 (1H, dd, *J* = 7.8, *J* = 1.4, H-8). ^{13}C NMR spectrum, δ, ppm: 23.7 (CH_3); 31.1 (CH_2); 39.9 (CH_2Ph); 116.7 (=CH_2); 121.3 (CH); 121.7 (C); 123.3 (C); 126.2 (CH); 126.4 (CH); 127.0 (CH); 127.6 (C); 128.5 (2CH); 128.7 (CH); 129.0 (2CH); 129.4 (CH); 131.8 (CH); 132.6 (CH); 133.6 (CH); 134.0 (CH); 140.7 (C); 144.3 (C); 147.8 (C); 152.6 (C); 160.2 (C(5)–O); 164.5 (O–C=O). Found, %: C 82.47; H 5.90; N 3.49. $C_{27}H_{23}NO_2$. Calculated, %: C 82.42; H 5.89; N 3.56.

Quinolone 5. ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (a) benzoyl, b) benzyl, c) butenyl groups): 2.33-2.46 (2H, m, H-2c); 2.61-2.71 (2H, m, H-1c); 4.27 (2H, s, C$\underline{H}_2$Ph); 4.94-5.05 (2H, m, =CH_2); 5.79 (1H, ddt, *J* = 16.9, *J* = 10.4, *J* = 6.4, H-3c); 7.12-7.29 (7H, m, H-2b-H-6b, H-3a, H-5a); 7.29-7.44 (2H, m, H-6, H-4a); 7.49 (1H, dd, *J* = 7.7, *J* = 1.0, H-6a); 7.61 (1H, dd, *J* = 8.4, *J* = 1.0, H-8); 7.70 (1H, ddd, *J* = 8.4, *J* = 6.9, *J* = 1.5, H-7); 8.00 (1H, dd, *J* = 8.1, *J* = 1.5, H-5); 11.94 (1H, br. s, NH). ^{13}C NMR δ, ppm: 30.7 (CH_2); 32.9 (CH_2); 38.0 ($\underline{C}H_2$Ph); 115.8 (=CH_2); 118.2 (CH); 120.7 (C); 123.8 (CH); 124.9 (C); 125.0 (CH); 125.8 (CH); 126.0 (CH); 128.2 (2CH); 129.0 (2CH); 129.8 (CH); 131.0 (CH); 131.2 (CH); 132.4 (CH); 136.8 (CH); 139.44 (C); 139.46 (C); 140.3 (C); 141.2 (C); 153.2 (C); 175.3 (C(4)=O); 198.8 (C=O). Found, %: C 82.51; H 5.82; N 3.55. $C_{27}H_{23}NO_2$. Calculated, %: C 82.42; H 5.89; N 3.56

The structures of **2** and **4** were additionally confirmed by X-ray diffraction structural analysis. The corresponding CIF files were deposited at the Cambridge Crystallographic Data Center (CCDC 740002 and CCDC 740003).

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