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NOVEL CONVERSION OF BUTYROLACTONES CONTAINING THE ORTHO-NITROPHENYL MOIETY TO INDOLES WITH TRIETHYL PHOSPHITE

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The triethyl phosphite-induced reductive cyclization of o-nitrobenzenes has been reported by many investigations.[1,2] Previously, the formation of the tricyclic oxazolo[5,4-b]quinoline (II) ring system from 4-(o-nitrobenzylidene)oxazolones (I) and triethyl phosphite was described.[3] Attempts to synthesize, in a similar manner, the naturally occurring furo[2,3-b]quinoline system from α-(o-nitrobenzyl)- and α-(α'-methoxy-o-nitrobenzylidene)butyrolactones, however, resulted in the formation of novel indole compounds.

Thus, treatment of α-(o-nitrobenzoyl)butyrolactone (III)[4] and α-(α'-methoxy-o-nitrobenzylidene)-butyrolactone (IV)[4] with a 4.7 and 5.0 equivalent excess of triethyl phosphite at 160 - 170° over 17 - 23 hr under nitrogen produced, respectively, the yellow spiro-indolinone lactone (V), m.p. 141 - 142°; blue fluorescence (in $CHCl_3$), ν max ($CHCl_3$) 3400 (NH), 1770 (lactone C=O), 1700 (C=O), 1610 cm^{-1} (Ar-$\underset{|}{N}$-$\overset{|}{C}R_1R_2$),[5] δ ($CDCl_3$) 2.69 (2H, dd, J = 8 and 3 Hz, X_2 part of ABX_2, CH_2CH_2O), 4.36 - 4.68 (1H, m, A part of ABX_2, CH_2CH_2O), 4.71 - 5.17 (2H, m, B part of ABX_2, CH_2CH_2O and NH, exchangeable with D_2O), 6.84 - 7.16 (2H, m, ArH), 7.43 - 7.84 ppm (2H, m, ArH), λ max (CH_3OH) 390,257,232 nm, m/e 203 (M^+), 159 ($M^+ - CO_2$), 130 (159 - CH_2CH_2 - H), 104 (130 - CN); and the colorless tricyclic indolo-lactone (VI), m.p. 65.5 - 66.5°; ν max ($CHCl_3$) 1730 cm^{-1} (C=O), δ ($CDCl_3$) 3.19 (2H, t, J = 6.5 Hz, CH_2CH_2O), 3.95 (3H, s, $ArOCH_3$), 4.48 (2H, t, J = 6.5 Hz, CH_2CH_2O), 7.13 - 7.64 (3H, m, ArH), 8.09 - 8.30 ppm (1H, m, aromatic C_7 - H), λ max (CH_3OH) 270,232 nm, m/e 217 (M^+), 202 ($M^+ - CH_3$), 173 ($M^+ - CO_2$), 158 (202 - CO_2 or 173 - CH_3), 130 (158 - CH_2-CH_2), 104 (130 - CN).

The spiro-indolinone lactone (V) is probably formed by a nitrene insertion process, and VI via a nitrene (VII) and an aziridine (VIII) intermediate followed by a rearrangement.

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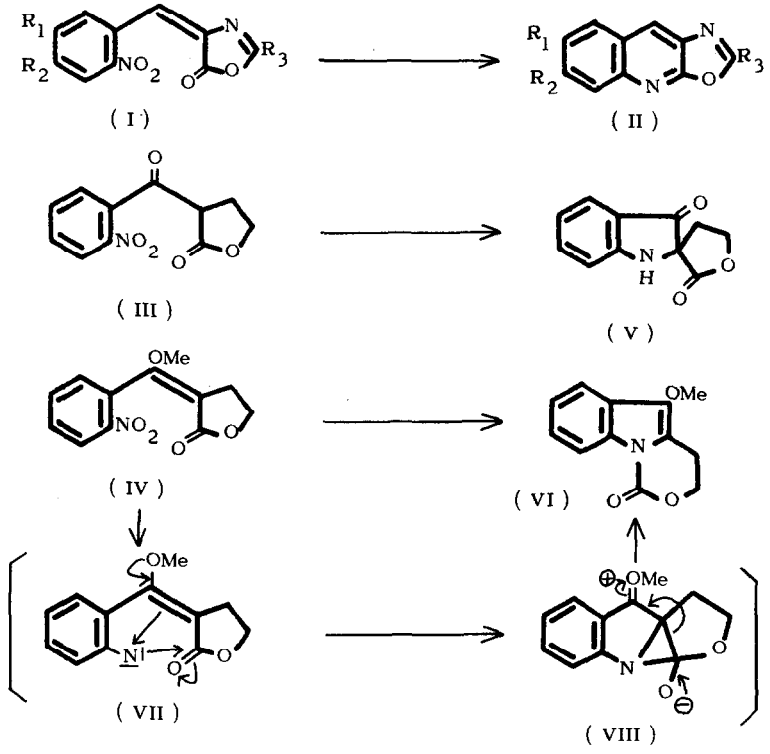
These unusual reaction products are being studied further. Compound V is of special interest because of its structural similarity to the natural product C-fluorocurine.[6]



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