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A NOVEL FORMATION OF 1-HYDROXYMETHYL-4,5-DIMETHOXY-7H-AZIRINO-[1,2-a]INDOLE-7a-CARBOXYLIC ACID γ-LACTONE

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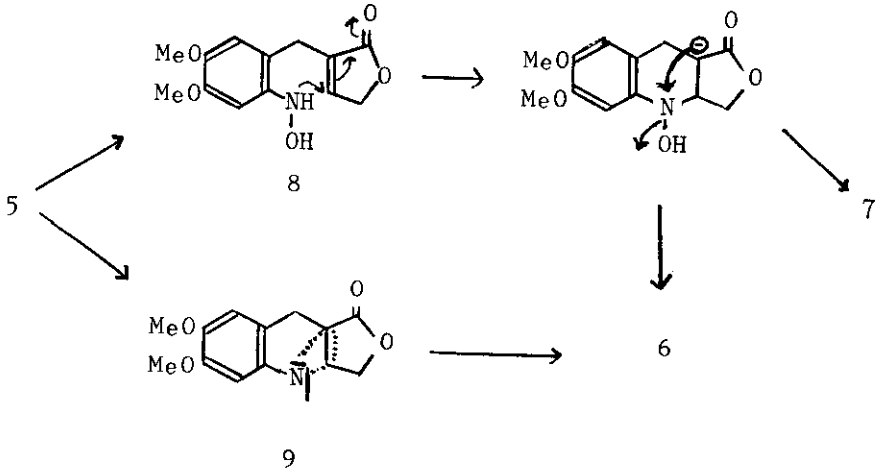
α-(6-Nitroveratrylidene)-γ-butyrolactone (1) rearranges to 3-(6-nitroveratryl)-2(5H)-furanone (5), and is deoxygenated to 1-hydroxymethyl-4,5-dimethoxy-7H-azirino[1,2-a]indole-7a-carboxylic acid γ-lactone (6) in triethyl phosphite at 140 - 150°. Although frequently postulated in triethyl phosphite reductions of nitro compounds, aziridines have not, heretofore, been isolated.

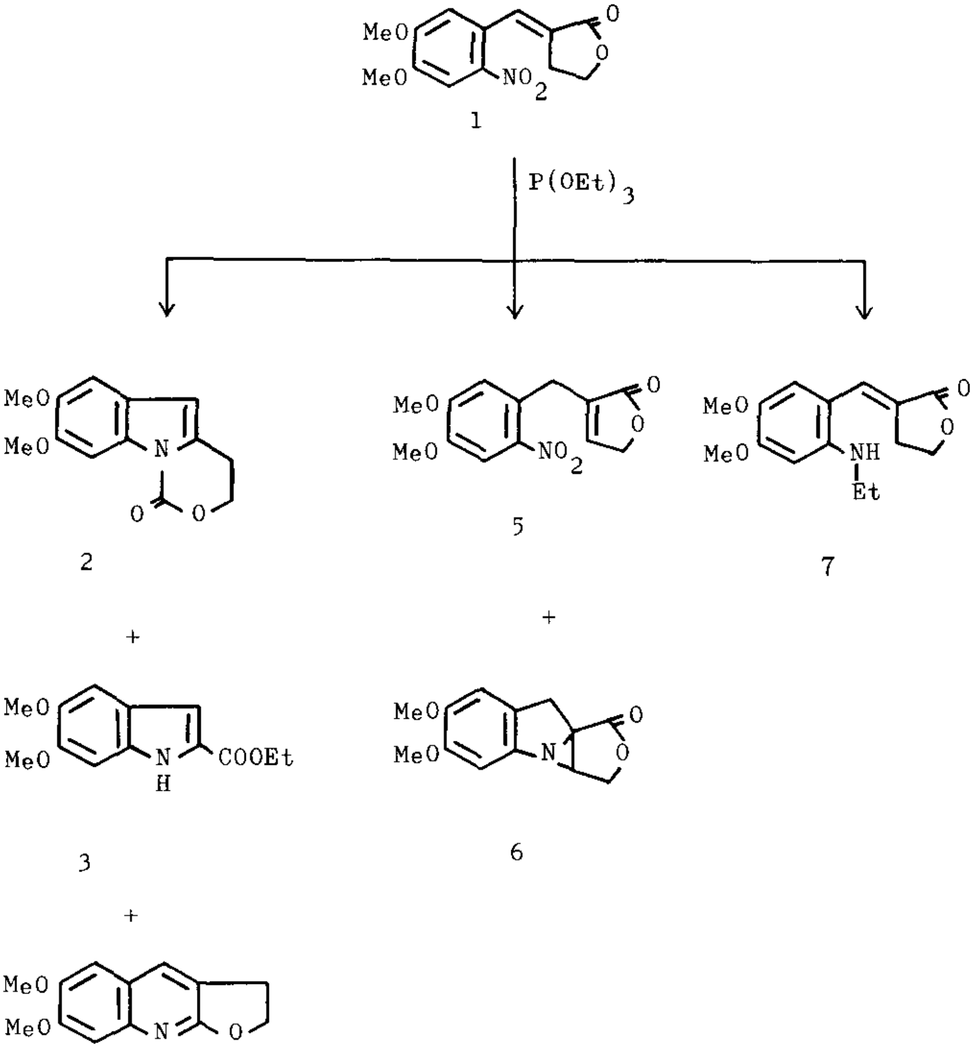
Deoxygenation of α-(6-nitroveratrylidene)-γ-butyrolactone (1) with triethyl phosphite at 140 - 150° over 5 hr afforded a mixture of six products and a trace of 1. In addition to 3,4-dihydro-7,8-dimethoxy[1,3]oxazino[3,4-a]indol-1-one (2) (3.7 %), ethyl 5,6-dimethoxyindole-2-carboxylate (3) (trace), and 2,3-dihydro-6,7-dimethoxyfuro[2,3-b]-quinoline (4) (<1 %), compounds obtained previously[2] at 160 - 165° after 20 hr, the following new compounds were isolated:

3-(6-Nitroveratryl)-2(5H)-furanone (5) (7.1 %), mp 122° (solidifies and remelts at

134°); uv (MeOH) 243, 300 sh, 340 nm; ir ($CHCl_3$) 1750 (C=O), 1580, 1500, 1325 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 3.93 and 3.98 (8H, s, 2 x OCH_3 and $ArCH_2$), 4.75 (2H, distorted d, *J* 1.5 Hz, $OC\underline{H}_2CH$), 7.02 (1H, s, Ar 2 - H), 7.18 (1H, distorted t, *J* 1.5 Hz, $OCH_2C\underline{H}$), 7.63 (1H, s, Ar 5 - H); m/e 279 (M^+), 262 (M^+ - OH), 233 (M^+ - NO_2); 1-hydroxymethyl-4,5-dimethoxy-7H-azirino[1,2-a]indole-7a-carboxylic acid γ-lactone (6) (3.5 %), mp 179 - 180°; uv (MeOH) 235, 290 nm; ir ($CHCl_3$) 1775 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.82 (1H, d, *J* 3 Hz, $NC\underline{H}CH_2$), 3.47 (2H, pair of d, *J* 18 Hz, $ArCH_2$), 3.78 (6H, s, 2 x OCH_3), 4.27 (1H, dd, *J* 10 and 3 Hz, $OC\underline{H}_2CH$), 4.45 (1H, d, *J* 10 Hz, $OC\underline{H}_2CH$), 6.66 and 6.73 (each 1H, s, ArH); m/e 247 (M^+), 232 (M^+ - Me), 203 (M^+ - CO_2), 188 (203 - Me or 232 - CO_2), 160 (188 - CH_2CH_2 or -CO); and α-(6-ethylaminoveratrylidene)-γ-butyrolactone (7) ($<$ 1 %), mp 131 - 134°; uv (MeOH) 240, 270, 305, 405 nm; (MeOH-HCl) 235, 295, 320 nm; ir ($CHCl_3$) 3435 (NH), 1730 (C=O), 1605 cm^{-1}; nmr ($CDCl_3$) δ 1.28 (3H, t, *J* 8 Hz, $CH_2C\underline{H}_3$), 2.05 (1H, br, NH exchangeable with D_2O), 3.16 (2H, q, *J* 8 Hz, $NHC\underline{H}_2CH_3$), 3.18 (2H, dt, *J* 3 and 8 Hz, $OCH_2C\underline{H}_2$), 3.74 and 3.83 (each 3H, s, 2 x OCH_3), 4.35 (2H, t, *J* 8 Hz, $OC\underline{H}_2CH_2$), 6.15 (1H, s, Ar 5 - H), 6.76 (1H, s, Ar 2 - H), 7.44 (1H, t, *J* 3 Hz, ArCH); *m/e* 277 (M^+), 262 (M^+ - Me), 260 (M^+ - OH), 141.

There are many pathways which could lead to lactone 7 and aziridine 6 on deoxygenation of 1. The plausible mechanisms are as follow; thus, 1 may be reduced to the hydroxylamine derivative (8), whose addition to the α,β-unsaturated lactone, followed by recyclization, gave the aziridine 6. In this case the reaction of 8 with ethanol would give the lactone 7. The other route to the aziridine 6 is the way that this reaction would proceed *via* a nitrene (9) which adds intramolecularly to an unsaturated lactone. Although aziridines have been suggested[2,3] as intermediates in the triethyl phosphite reduction of nitroaromatics, there appear to be no other cases of their isolation. Intermolecular addition of a nitrene, generated from a nitroso-aromatic, to olefins was reported to give aziridines.[4]




1
P(OEt)3
2
3
5
6
7
+
MeO
NO2
NH
Et
COOEt
N
H
O

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