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Ready Alcoholysis of the Cycloadducts (Urazole) of 4-Phenyl-1,2,4-triazole-3,5-dione by Solvent-assisted Backbone Participation

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A series of urazoles containing $\alpha\beta$ -carbonyl groups underwent ready alcoholysis by solvent-assisted backbone participation in the presence of potassium hydroxide to give oxazolinones.

Although 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) shows a diversity of reactions with alkenes, *e.g.* [4 + 2],^{1,2} [2 + 2],² ene,^{3,4} and dipolar reactions,⁵ to afford unique adducts (urazole), use of the latter has been limited.⁶⁻⁸ This is probably because the urazole ring is difficult to open and relatively drastic conditions are needed to accomplish it (*e.g.* KOH in refluxing MeOH¹ or PrⁱOH);⁹ hydrazine in ethanol has, however, been recommended for the mild hydrolysis of strained urazoles.¹⁰

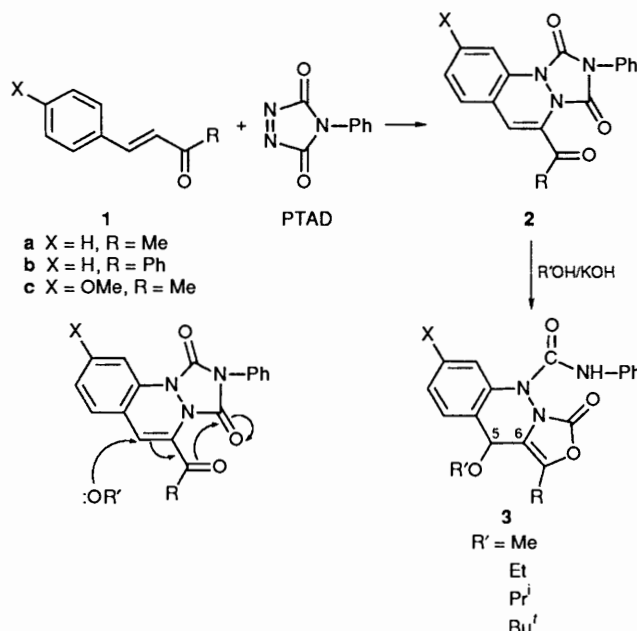
Here, we report that the urazoles arising from the reaction of a variety of styryl ketones with PTAD,¹¹ were readily cleaved by solvent-assisted participation of the neighbouring β -carbonyl group (backbone participation) under mild conditions to give new bicyclic oxazolinones.

As reported previously,¹¹ benzylideneacetone **1a** reacted with PTAD to give **2a** (27%) via an addition-elimination mechanism. Treatment of an ethanolic solution of **2a** with powdered KOH for 30 min at 25 °C, resulted in loss of the characteristic colour. Work-up of the solution (neutralization by dilute HCl and recrystallization from EtOH), gave white needles of **3a** (77%). The oxazolinone structure was assigned on the basis of spectral evidence: δ_{H} 1.72, 5.35 and 6.54 [Me, olefinic (5-H), and amide protons] in addition to ethoxy protons; δ_{C} 79.7 (d, C-5) and 154.0 and 154.5 (both s, CONH₂). The mass and the IR spectra and elemental analyses supported the proposed structure. It is suggested that the facile ring-opening under mild conditions proceeds by solvent-assisted participation of a neighbouring and enolizable carbonyl group (see Scheme 1).

Similar reactions (see Table 1) gave a series of oxazolinones the structures of which were also assigned on the basis of the elemental analyses and spectral evidence. Starting material was, however, recovered for entry 4, presumably because of the low nucleophilicity and steric bulkiness of the *tert*-butoxy group.

Experimental

Synthesis of the Oxazolinone 3a.—To a suspension of compound **2a** (164 mg, 0.50 mmol) in ethanol (20 ml) was added powdered potassium hydroxide (200 mg, 3.6 mmol). The solution was stirred (magnetic stirrer) for 30 min at 25 °C during which time the characteristic yellow colour disappeared. The solution was diluted with water (50 ml) and neutralized by hydrochloric acid (2 mol dm⁻³) to give a white precipitate. This was filtered off by suction and recrystallized (ethanol) to give **3a** (77%) as colourless needles; m.p. 109–110 °C; δ_{H} (60 MHz; CDCl₃) 1.41 (3 H, t, CH₃), 1.72 (3 H, s, CH₃), 3.80 (2 H, q, CH₂), 5.35 (1 H, s, 5-H), 6.54 (1 H, s, NH) and 7.08–7.54 (9 H, m, Ph); δ_{C} (200 MHz; CDCl₃) 15.4(q), 21.0(q), 68.1(t), 79.7(d), 86.1(s), 96.9(s), 116.3(d), 125.2(d), 125.3(d), 127.7(d), 128.2(d), 129.2(d), 129.9(s), 130.7(d), 133.9(d), 139.3(s), 154.9(s) and 154.5(s); ν_{max} (KBr)/cm⁻¹ 3320, 1763, 1712, 1610, 1124 and



Scheme 1 Alcoholysis of urazole with backbone participation

Table 1 Preparation of oxazolinones 3 by backbone participation

Entry	X	R	R'	Yield of 3(%) ^a
1	H	Me	Me	76
2	H	Me	Et	77
3	H	Me	Pr ⁱ	23
4	H	Me	Bu ^t	0
5	H	Ph	Et	65
6	H	Ph	Pr ⁱ	60
7	OMe	Me	Et	50

^a Based on 2.

1104; *m/z* (%) 365 (100, M⁺), 321 (30), 276 (36), 200 (24) and 158 (14) (Found: C, 65.9; H, 5.16; N, 11.6. C₂₀H₁₉N₃O₄ requires C, 65.72; H, 5.24; N, 11.51%).

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