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Novel Base-promoted Addition–Elimination Reaction of Electron-deficient Benzylidene Derivatives with *N*-Phenyl-1,2,4-triazole-3,5-dione (PTAD)

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The reaction of electron-deficient benzylidene derivatives with PTAD afforded the double Diels–Alder product and the Diels–Alder ene product; the latter underwent novel base-induced elimination of phenyl urazole *via* a stable carbanion.

While *N*-phenyl-1,2,4-triazole-3,5-dione (PTAD) has been used extensively in organic syntheses, and a diversity of reactions with alkenes have been documented, *e.g.* [4 + 2],[1] [2 + 2],[2] ene[3] and dipolar reactions,[4] no studies have described reactions involving potent leaving groups. We found that the urazoyl group (NHCONHNHCO; phenyl substituted) served as a good leaving group in the reaction products of PTAD with benzylidene derivatives containing carbonyl or ester groups.

The reaction of 1-phenylpent-1-ene-3-one **1b** with PTAD in methylene chloride at 25 °C afforded the double Diels–Alder

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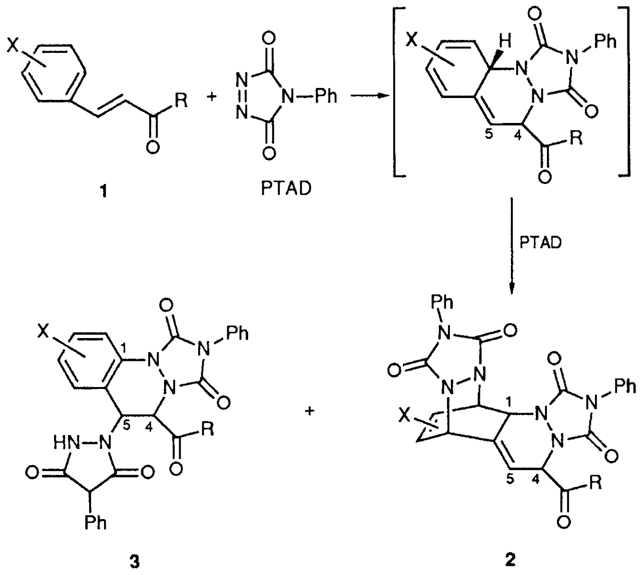
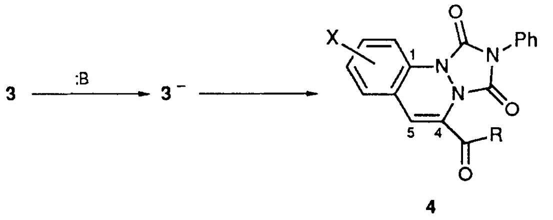


Scheme 1 Reaction of PTAD with benzylidene derivatives



Scheme 2 E_1cb mechanism

product **2b** and the Diels–Alder ene product **3b** *via* a mono-Diels–Alder intermediate in isolated yields of 27 and 24%, respectively (Scheme 1). However, the Diels–Alder ene product partially decomposed during purification (silica gel chromatography and recrystallization). Careful recrystallization from acetonitrile gave pure **3b** as a white powder, m.p. 139–140 °C. Spectral data and elemental analyses supported the proposed structure. The ^{1}H NMR spectrum showed two doublet signals at δ 5.33 and 6.02 corresponding to 4- and 5-H, respectively. The ^{13}C NMR spectrum also showed two doublet signals at δ 52.7 and 63.9. The mass spectrum showed M^+ at m/z 510. When a catalytic amount of triethanolamine was added to an acetonitrile solution (10 ml) of **3b** (158 mg) at 25 °C, the solution turned yellow in a few minutes to afford yellow crystals of **4b** in 94% yield after conventional purification, m.p. 183–184 °C. This structure was also assigned on the basis of spectral and elemental analyses. The ^{1}H NMR spectrum showed a singlet proton signal at low field (δ 6.21) in addition to ethyl (δ 1.25 and 2.32) and phenyl signals (δ 7.03–7.69). Compound **4b** resulted from novel base-induced elimination of urazoyl·H. This elimination can be carried out *in situ* without isolation of **3b**.

Table 1 Product yields of **4** from addition–elimination *in situ*

Benzylidene derivative			Yield (%) of **4**[a]
	X	R	
1a	H	Me	27
1b	H	Et	34
1c	H	Ph	16
1d	*p*-OMe	Me	52
1e	*p*-OMe	OEt	27
1f	*p*-OMe	Ph	61
1g	*p*-Cl	Me	26
1h	*o*-Cl	Me	33

[a] Yield based on **1**.

The *in situ* reaction was extended to a series of benzylidene derivatives containing electron-attracting groups (carbonyl and ester). As shown in Table 1, similar successive addition–elimination reactions took place in all cases.

In order to elucidate the mechanism of elimination in particular, the deuterium exchange reaction of **3b** was studied by ^{1}H NMR spectroscopy in $CDCl_3$ in the presence of deuterium oxide and a catalytic amount of sodium carbonate. Addition of sodium carbonate caused immediate exchange at C-4 more rapidly than formation of **4**. Furthermore, the recovered starting material was completely deuteriated at C-4. These findings suggest that the elimination reaction may proceed *via* a carbanion as shown in Scheme 2. Presumably, the electron-attracting carbonyl or ester and urazoyl groups each stabilize the conjugate base of **3**. In summary, the urazoyl group is a good leaving group in eliminations *via* carbanions.

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