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## Key indicators

 Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
 R factor = 0.031  
 wR factor = 0.089  
 Data-to-parameter ratio = 8.4

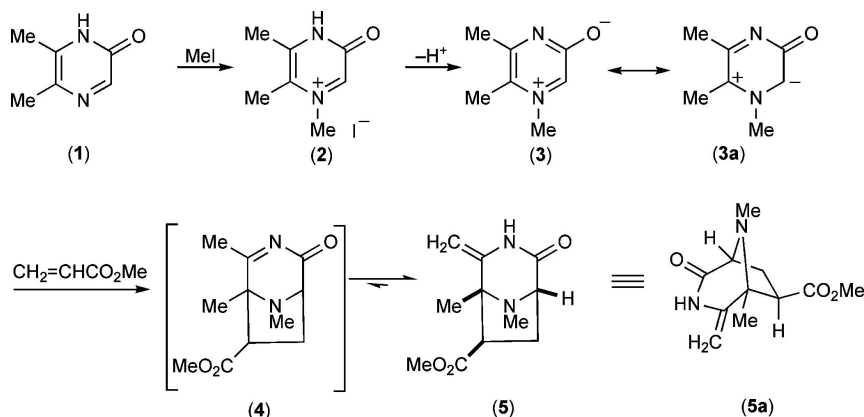
 For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

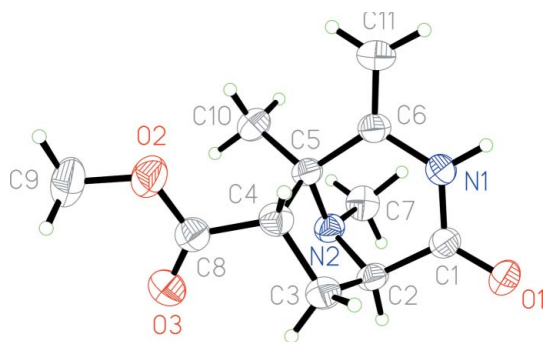
 The dipolar cycloaddition of methyl acrylate  
 to 1,5,6-trimethyl-3-oxidopyrazinium

 5,6-Dimethylpyrazin-2-one reacts with iodomethane to give a quaternary salt, deprotonation of which liberates a 3-oxidopyrazinium which undergoes a 1,3-dipolar cycloaddition with methyl acrylate to form methyl 5,8-dimethyl-4-methylene-2-oxo-3,8-diazabicyclo[3.2.1]octane-6-*exo*-carboxylate,  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_3$ , as the major product.

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## Comment

 We have been investigating the 1,3-dipolar cycloaddition chemistry of 3-oxidopyraziniums (Kiss *et al.*, 1987; Allway *et al.*, 1990; Yates *et al.*, 1995). These reactions efficiently produce bridged bicyclic systems, *viz.* 3,8-diazabicyclo[3.2.1]octanes, which comprise key structural components of such biologically active natural products as anticancer quinocarcin (Takahashi & Tomita 1983; Tomita *et al.*, 1983; Hirayama & Shirahata, 1983) and antibiotic lemomycin (He *et al.*, 2000). Our studies were initially inspired by the series of benchmark papers by Katritzky and co-workers [for reviews, see Dennis *et al.* (1976) and Katritzky & Dennis (1989)] on the cycloadditions of 3-oxidopyridiniums. In neither Katritzky's extensive studies nor our own on 3-oxidopyraziniums had the possible influence of a substituent on the 1,3-dipole at one (or both) of the future ring-junction positions been assessed. This report describes our first study to remedy this omission, in which the reactivity of 1,5,6-trimethyl-3-oxidopyrazinium, (3) (see scheme; synthesis of 1,5,6-trimethyl-3-oxidopyrazinium and its reaction with methyl acrylate), was assessed.

 5,6-Dimethylpyrazin-2-one, (1) (Jones, 1949; Karmas & Spoerri, 1952), was reacted with iodomethane to produce the methiodide (2), treatment of which with triethylamine allowed the generation of the zwitterion (3), *in situ* and in the presence of methyl acrylate. The reactivity and regioselectivity of such 3-oxidodiaziniums is easily understood in terms of a resonance contributor [(3a) in this case]. The immediate products of the



**Figure 1**  
Plot of (4), with displacement ellipsoids drawn at the 50% probability level.

cycloadditions [(4) in this case] are not isolated, but tautomerize to the enamide structure [(5) in this case], (5a) showing better the bicyclic nature of the product. A mixture of two isomeric products was formed from which the major isomer was isolated, crystalline, allowing an X-ray analysis to show that it was the *exo*-ester (4) (Fig. 1). Thus, the additional oxidopyrazinium-6-methyl, appearing at the ring junction (C-5) in the cycloadduct, did not affect the efficiency or stereoselectivity of the cycloaddition, compared with the comparable reaction of 1,5-dimethyl-3-oxidopyrazinium which also gave a 6-*exo*-ester as the major product (Yates *et al.*, 1995).

## Experimental

5,6-Dimethylpyrazin-2-one (Jones, 1949; Karmas & Spoerri, 1952) (800 mg, 6.5 mmol) and iodomethane (2 ml, 32.5 mmol, 5 equivalents) were heated under reflux in MeCN (150 ml) under nitrogen for 24 h. The solvent was evaporated under vacuum and the residue extracted with  $\text{CH}_2\text{Cl}_2$ . Insoluble material was removed by filtration and the solution evaporated, leaving 3,4-dihydro-1,5,6-trimethyl-3-oxopyrazinium iodide as a dark-brown crystalline solid (1.12 g, 66%; m.p. >523 K);  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ , 300 MHz,  $\delta$ , p.p.m.): 8.20 (1H, s, C2-H), 4.15 (3H, s, NMe), 2.50 and 2.45 (2  $\times$  s, 2  $\times$  3H, 2  $\times$  CMe). Analysis found: C 32.31, H 4.02, N 10.39%;  $\text{C}_7\text{H}_{11}\text{N}_2\text{O}$  requires: C 31.60, H 4.17, N 10.53%

A solution of 3,4-dihydro-1,5,6-trimethyl-3-oxopyrazinium iodide (1.5 g, 5.6 mmol),  $\text{Et}_3\text{N}$  (1.6 ml, 11.2 mmol, 2 equivalents), and methyl acrylate (1.52 ml, 16.8 mmol, 3 equivalents) in dry MeCN (100 ml) was heated under reflux for 2 h. Solvents were removed from the resulting orange solution under vacuum,  $\text{H}_2\text{O}$  (30 ml) was added and the product extracted into  $\text{CH}_2\text{Cl}_2$  (3  $\times$  30 ml). The combined dried extract was evaporated leaving a brown oil (0.88 g, 70%) from which, by careful chromatography over silica, eluting with *n*-hexane–EtOAc (1:1), the major (thin-layer chromatography) adduct was obtained as colourless plates (330 mg, 26%; m.p. 383–388 K).

### Crystal data

$\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_3$	$D_x = 1.330 \text{ Mg m}^{-3}$
$M_r = 224.26$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 17414 reflections
$a = 9.818 (10) \text{ \AA}$	$\theta = 2.1\text{--}25.0^\circ$
$b = 7.89 (2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 14.80 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 102.23 (8)^\circ$	Plate, colourless
$V = 1120 (4) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.1 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku R-Axis II diffractometer	$R_{\text{int}} = 0.037$
$\varphi$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: none	$h = 0 \rightarrow 11$
17414 measured reflections	$k = 0 \rightarrow 9$
1767 independent reflections	$l = -17 \rightarrow 16$
1516 reflections with $I > 2\sigma(I)$	

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.1608P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
1767 reflections	$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$
210 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.037 (6)

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{N1---H1}\cdots\text{O1}^i$	0.913 (18)	2.082 (19)	2.980 (6)	167.6 (15)

Symmetry code: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .

H atoms were found by difference Fourier methods and refined isotropically, with refined C–H distances in the range 0.932 (15)–1.041 (19)  $\text{\AA}$  and an N–H distance of 0.913 (18)  $\text{\AA}$ .

Data collection: *MSC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *DENZO* (Otwinowski & Minor, 1987); data reduction: *DENZO*; program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *TEXSAN* (Molecular Structure Corporation, 1995).

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