Reactions of Xanthinium *N*(7)-Ylides with Olefinic Dipolarophiles

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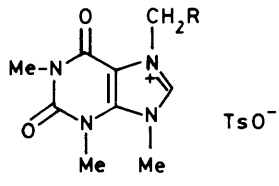
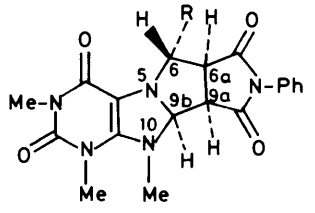
The stereo- and regio-chemical aspects of the reactions of xanthinium *N*(7)-methylides (**2**) with olefinic dipolarophiles were elucidated. The reactions of ylides (**2**) with *N*-phenylmaleimide afforded stereoselective *endo* adducts, and with acrylates and acrylonitrile afforded stereo- and regio-selective 6-*endo* adducts. On the other hand, the reactions of ylides (**2**) with *trans*-olefins afforded mixtures of two stereoisomers, the 8-*endo*-7-*exo* and 8-*exo*-7-*endo* pyrrolo[2,1-*f*]purine derivatives. Stereochemistry of the adducts was elucidated by ^{1}H n.m.r. and *X*-ray analysis. The stereoselectivity of the adducts was governed by the balance of steric and electronic effects. The ylides (**2**) reacted in their *Z*-form in all reactions investigated. The steric factors of the dipolarophiles were also closely examined.

1,3-Dipolar cycloadditions of azomethine ylides with olefinic dipolarophiles have been actively studied.[1,2] Stereo- and regiochemical control of this addition is indispensible for the application of the reaction to organic syntheses, especially to natural product synthesis.[3] It is of interest to investigate the factors influencing the stereochemistry of these cycloaddition reactions. For the discussion of stereoselectivity of the cycloaddition reaction, determination of stereochemistry is important.[4] The stereostructures of the adducts have been determined mainly on the basis of the ^{1}H n.m.r. spectral data, but some structures were misassigned.[5,6] Recently, Bende *et al.* reported the stereochemistry, as evidenced by *X*-ray analysis, of the adduct obtained from 3,4-dihydroisoquinolinium methylide with an olefinic dipolarophile.[7] We previously reported the generation of xanthinium *N*(7)-methylides (**2**)† and their nature as 1,3-dipoles in the reaction with acetylenic dipolarophiles.[8] We now report the stereo- and regio-chemistry of the reactions of ylides (**2**) with various olefinic dipolarophiles as determined by the steric and electronic nature of substituents in the 1,3-dipoles and dipolarophiles.[9]



(**1**) (**2**)



(**3**)

a, R = CN; **b**, R = CO_2Me; **c**, R = COPh; **c'**, R = COC_6H_4Br-*p*; **d**, R = COC_6HMe_4-2,3,5,6

Results

Reactions of Xanthinium N(7)-*Methylides* (**2**) *with* cis-*Symmetric Olefins.*—The *N*(7)-xanthinium toluenesulphonates (**1a**—**d**) were suspended in dry MeCN containing 1 mol equiv. of dipolarophile, and treated with triethylamine at room temperature. The reactions of ylides (**2a**—**c**) with *N*-phenylmaleimide gave only 1:1 adducts (**3a**—**c**) in good yield. These products were stable and were purified by recrystallisation from appropriate solvents (Table 8). The stereochemistry of these adducts was assigned from the ^{1}H n.m.r. coupling constants of the pyrrolidine rings[10,11] (Table 1). The coupling constants between 6a-H and 6-H (1.0—1.2 Hz) confirm the *trans* relationship of these hydrogens, and those between 9a-H and 9b-H (6.4—7.8 Hz) show a *cis* relationship. Thus, the products (**3a**—**c**) were assigned as being *endo* (3 + 2) adducts. The reactions of ylides (**2a**—**c**) with other *cis*-olefins, such as dimethyl maleate, *cis*-1,2-dibenzoylethylene, or maleic anhydride, afforded no adduct but only hydrolysis products[8] (**7a**—**c**). When reaction of ylide (**2b**) with dimethyl maleate was conducted in tetrahydrofuran (THF) with n-butyl-lithium as a base, the only product isolated was the pteridine derivative (**6**) in 49.7% yield. The structure of compound (**6**) was determined from the ^{1}H n.m.r. data which showed the presence of two OMe groups and an allylic proton. The stereochemistry between 3a-H and 3-H was determined to be *trans* from the coupling constant (*J* 5.7 Hz). The formation of compound (**6**) can be explained if at first an *endo* adduct (**4**) is formed, followed by ring-opening and recyclisation of intermediate (**5**) with the loss of methanol[8] to give the product (**6**) (Scheme 1).

Reactions of Ylides (**2**) *with Acrylic Acid Derivatives.*—The reactions of ylides (**2a**—**c**) with acrylates were conducted under the same reaction conditions as noted above. The products obtained were solely 6-*endo*-isomers (**8**)—(**10**) (Table 2). The regiochemistry of the adducts was chemically elucidated by dehydrogenation. Treatment of the adduct (**10c**), obtained from the reaction of (**2c**) with ethyl acrylate, with 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil) in benzene afforded a dehydrogenated product, ethyl 6-benzoyl-1,3,9-trimethyl-2,4-dioxo-2,3,4,9-tetrahydro-1*H*-pyrrolo[2,1-*f*]purine-8-carboxylate (**11**).

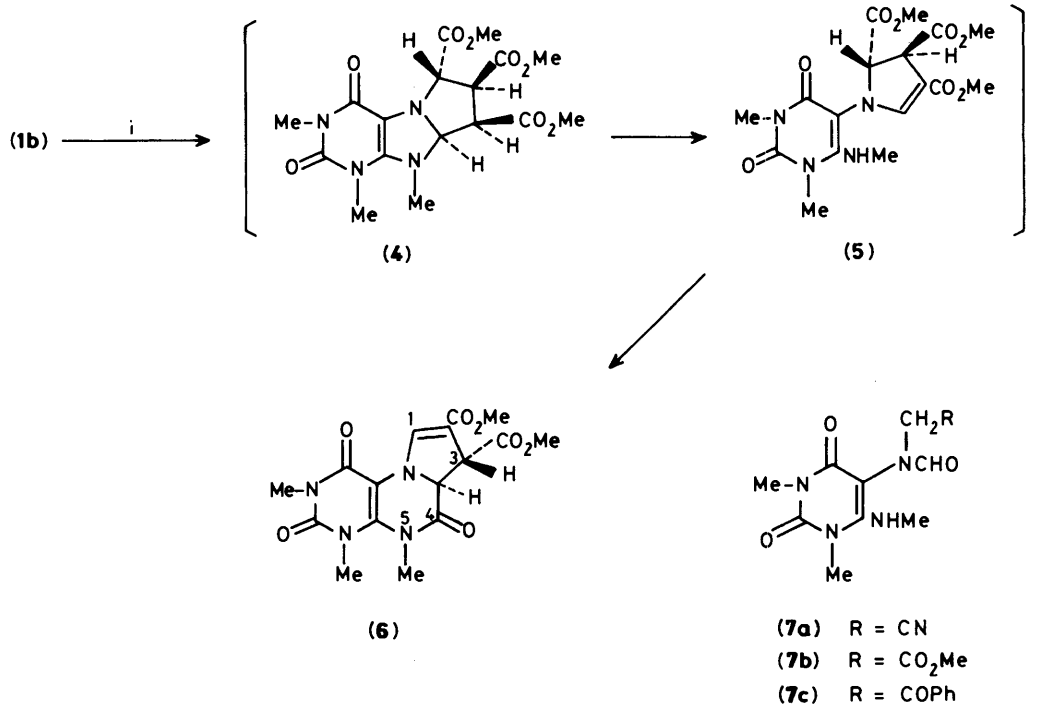
The coupling constants of the pyrrolidine ring of compound (**10c**) were $J_{6,7}$ 7.1 Hz, $J_{6,7'}$ 1.2 Hz, $J_{7,8}$ 11.0 Hz, $J_{7',8}$ 8.2 Hz, and

† Xanthine (a IUPAC non-allowed trivial name) will be used throughout this paper for convenience. The systematic name is purine-2,6(1*H*,3*H*)-dione.

Table 1. Reaction of ylides (**2**) with *N*-phenylmaleimide

Product	Yield	^{1}H N.m.r. (δ)[a] 6a-H ($J_{6a,6}$)	9a-H ($J_{9a,6a}$)	9b-H ($J_{9b,9a}$)	6-H	10-Me	1-Me	3-Me	Others	*m/z* M^+	Rel. int. Base
(**3a**)	Quant.	3.84 (1.0)	3.93 (8.3)	5.43 (7.8)	5.80	3.18	3.24	3.31	6.89—7.43 (5 H, m, Ph)	406	233
(**3b**)	83.4%	3.75 (1.0)	3.84 (8.4)	5.45 (7.6)	5.53	3.14	3.24	3.31	3.84 (OMe), 6.91—7.43 (5 H, m, Ph)	439	266
(**3c**)	Quant.	3.91 (1.2)	3.96 (8.4)	5.21 (6.4)	6.54	3.16	3.25	3.38	6.96—7.64 (8 H, m, ArH), 8.49—8.54 (2 H, m, ArH)	485	174

[a] 200 MHz.



Scheme 1. *Reagents:* i, (*Z*)-$MeO_2CCH{=}CHCO_2Me$, Bu^{n}Li

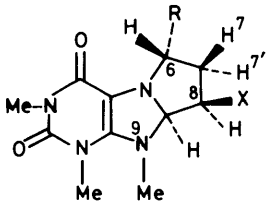
Table 2. Reactions of ylides (**2**) with acrylic acid derivatives ($CH_2{=}CHX$)

Olefin X	Ylide	Product	Yield (%)	Coupling constant[a] (Hz) $J_{6,7}$	$J_{6,7'}$	$J_{8,8a}$
CN	(**2a**)	(**8a**)	35.0	*b*	*b*	6.7
	(**2b**)	(**8b**)	93.5	6.9	3.9	6.0
	(**2c**)	(**8c**)	97.0	6.9	1.0	6.9
CO_2Me	(**2a**)	(**9a**)	25.7	6.9	3.8	7.1
	(**2b**)	(**9b**)	24.0	6.6	3.3	7.1
	(**2c**)	(**9c**)	67.0	5.9	2.7	8.0
CO_2Et	(**2a**)	(**10a**)	18.2	6.8	4.6	6.8
	(**2b**)	(**10b**)	28.0	7.4	3.2	7.2
	(**2c**)	(**10c**)	77.0	7.1	1.2	8.1

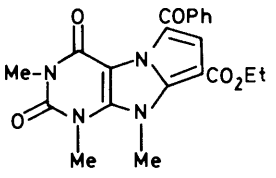
[a] 200 MHz for (**10c**) and 60 MHz for the others. [b] *J*-Values were not measurable because of signal overlap.

$J_{8,8a}$ 8.1 Hz from the 200 MHz ^{1}H n.m.r. spectrum. From these values the structure of compound (**10c**) was assigned as 6-benzoyl-1,3,9-trimethyl-2,4-dioxo-2,3,4,6,7,8,8a,9-octahydropyrrolo[2,1-*f*]purine-8-carboxylate, *i.e.* the 6-*endo* product. Similarly other adducts, (**8**), (**9**), (**10a** and **b**), were assigned as being 6-*endo* products. The ylides reacted stereoselectively in the *anti* form. In the case of less reactive dipolarophiles, hydrolysis of the ylides occurred preferentially and the adducts were formed in lower yields (**8a**), (**9a** and **b**), (**10a** and **b**).

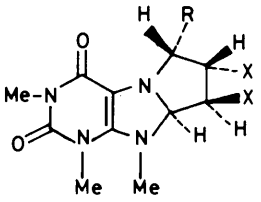
Reactions of Ylides (**2**) *with* trans-*Symmetric Olefins.*[9]—The reactions of the ylides with various *trans*-symmetric olefins gave mixtures of two stereoisomers, 8-*endo*-7-*exo* [(**12**)—(**15**), Type I] and 8-*exo*-7-*endo* adducts [(**16**)—(**19**), Type II], which were separated by column chromatography. The results are shown in Table 3. The stereochemistry of each product was determined from the coupling constants of hydrogens (8a-, 8-, 7-, and 6-H) on the newly formed pyrrolidine rings as described above. Further support of our stereostructural assignment was obtained from the differences of the chemical shifts of the N(9)–Me peaks between compounds of Type I and Type II as shown in Table 4. The N(9)–Me peaks of Type-I compounds were lowered by 0.09—0.20 p.p.m. compared with those of Type-II isomers because of the deshielding effect of electron-withdrawing groups (X) at the 8-*endo* position. Furthermore, an *X*-ray analysis of the Type-I adduct (**14c'**), derived from



(8) X = CN
(9) X = CO_2Me
(10) X = CO_2Et

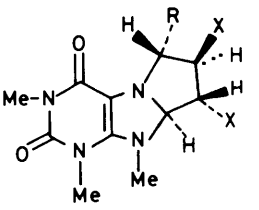


(11)



8-*endo*-7-*exo*; Type I

(12) X = CN
(13) X = COPh
(14) X = CO_2Me
(15) X = CO_2Ph

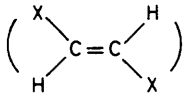


8-*exo*-7-*endo* ; Type II

(16)
(17)
(18)
(19)

a, R = CN; **b**, R = CO_2Me; **c**, R = COPh; **c'**, R = COC_6H_4Br-*p*; **d**, R = COC_6HMe_4-2,3,5,6

Table 3. Reactions of ylides (2) with *trans*-symmetric olefins



Olefin X	Ylide	Product yield (%) Type I	Type II
CN	(2a)	(12a) 60.4	
	(2b)	(12b) 62.0	
	(2c)	(12c) Quant.	
	(2d)	(12d) 59.6	(16d) 25.8
COPh	(2a)	(13a) 60.0	
	(2b)	(13b) 65.4	
	(2c)	(13c) 79.4	
	(2d)		(17d) 87.0
CO_2Me	(2a)	(14a) 45.8	(18a) 45.8
	(2b)	(14b) 67.3	(18b) 26.3
	(2c)	(14c) 54.0	(18c) 36.7
	(2c')	(14c') 61.7	(18c') 23.0
	(2d)		(18d) 62.4
CO_2Ph	(2a)	(15a) 63.4	(19a) 29.9
	(2b)	(15b) 54.6	(19b) 29.2
	(2c)		(19c) 86.2
	(2d)		(19d) 81.2

compound (**1c'**) (R = *p*-bromobenzoyl) with dimethyl fumarate, was conducted. The ORTEP drawing of compound (**14c'**) is shown in the Figure.[12]

On the basis of the stereostructure of adduct (**14c'**), the *cis* vicinal-proton coupling constants in the newly formed 5-membered ring were between 6.1 and 8.6 Hz and the *trans* ones were between 0 and 6.1 or > 8.6 Hz (Table 4).

The solvent effects in the reaction of ylide (**2c**) and dimethyl fumarate were investigated (Table 5). Although the reaction rate depended on the solubility of compound (**1c**) in the solvents tested, the ratios of Type-I (**14c**) and -II (**18c**) products were almost constant at 6:4.

Discussion

The conformation of the azomethine ylides is one of the important factors which determine the stereoselectivity of formation of the cycloadducts. The predominance of *anti* (cisoid) form over *syn* (transoid) form of dihydroisoquinolinium ylide and pyridinium ylide was explained by electrostatic attraction,[7d,13] but the energy differences between *anti*- and *syn*-ylides were estimated to be relatively small by CNDO/FORCE calculations.[7d]

Although the xanthinium ylides (**2a**—**d**) might possibly exist as the two conformers 2A (*syn*) and 2B (*anti*), only form 2B reacted as a 1,3-dipole in all the reactions. The steric and electronic repulsions between the carbonyl group at C-1 and the

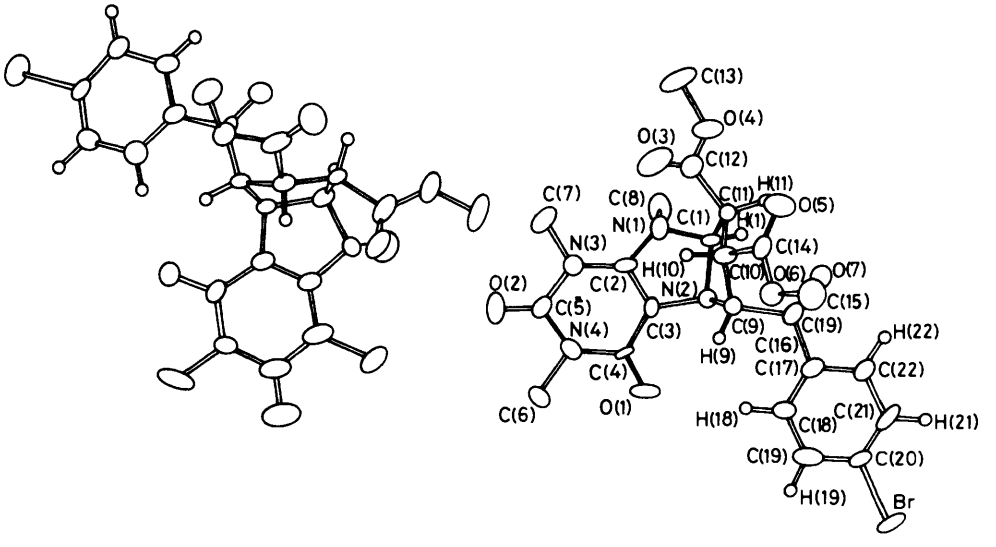


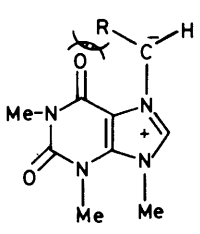
Figure. ORTEP drawing of compound (**14c'**) with crystallographic numbering scheme

Table 4. Spectral data of adducts (**12**)—(**19**)

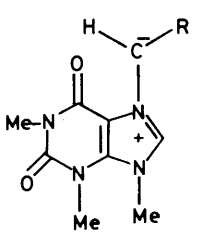
	^{1}H N.m.r. (δ)								
Compd.	8a-H ($J_{8,8a}$)	6-H ($J_{6,7}$)	7-H ($J_{7,8}$)	8-H	9-Me	1-Me	3-Me	Others	*m/z* M^+
(**12a**)[d]	5.39 (6.6)	5.34 (6.9)	3.42 (10.8)	3.47	3.22	3.31	3.53		311
(**12b**)[d]	5.44 (6.9)	5.13 (6.9)	3.21 (11.0)	4.03	3.18	3.31	3.53	3.86 (OMe)	344
(**12c**)[d]	5.17 (7.3)	6.26 (6.1)	3.34 (10.8)	4.31	3.17	3.39	3.55	7.54—8.42 (5 H, m, Ph)	390
(**12d**)[e]	5.10 (5.9)	5.80 (6.9)	3.77 (3.0)	3.46	3.10	3.25	3.43	2.22 (12 H, m, 4 × Me), 6.97 (1 H)	446
(**16d**)[e]	5.27 (5.2)	5.72 (6.3)	3.26 (2.3)	4.22	3.19	3.24	3.51	2.13—2.43 (12 H, m, 4 × Me), 6.97 (1 H)	446
(**13a**)[a]	*f* (6.8)	5.78 (7.5)	*f* (9.3)	*f*	2.42	3.22	3.31	7.40—7.80, 7.95—8.40 (10 H, m, Ph)	467
(**13b**)[a]	*g* (6.8)	5.84 (7.2)	*g* (13.8)	*g*	2.44	3.22	3.33	3.54 (OMe), 7.40—7.70, 7.90—8.20 (10 H, m, Ph)	502
(**13c**)[e]	5.54 (8.6)	6.45 (7.3)	4.90 (10.0)	5.32	2.45	3.20	3.43	7.25—8.25 (15 H, m, Ph)	548
(**17d**)[a]	5.43 (5.7)	5.68 (4.2)	4.65 (6.0)	4.85	2.84	3.28	3.48	1.99—2.30 (12 H, 4 × Me), 6.83 (1 H), 7.15—8.15 (10 H, m, Ph)	498
(**14a**)[e]	5.13 (7.3)	5.33 (7.6)	3.72 (11.6)	3.94	2.99	3.29	3.37	3.79, 3.81 (2 × OMe)	377
(**18a**)[e]	5.19 (5.7)	4.56 (7.6)	3.75 (8.9)	3.58	3.12	3.29	3.48	3.77, 3.84 (2 × OMe)	377
(**14b**)[b]	5.41 (7.3)	4.93 (7.3)	3.61 (11.5)	3.99	2.97	3.29	3.37	3.69, 3.72, 3.77 (3 × OMe)	410
(**18b**)[a]	5.28 (5.3)	4.54 (7.3)	*h*	*h*	3.13	3.31	3.52	3.75, 3.83, 3.86 (3 × OMe)	410
(**14c**)[e]	5.13 (8.6)	6.13 (7.0)	3.74 (10.8)	4.18	2.94	3.36	3.38	3.52, 3.79 (2 × OMe), 7.51—8.45 (5 H, m, Ph)	456
(**18c**)[e]	5.20 (4.6)	6.16 (2.4)	3.79 (4.6)	3.87	3.12	3.33	3.47	3.65, 3.83 (2 × OMe), 7.49—8.34 (5 H, m, Ph)	456
(**14c'**)[a]	5.12 (8.4)	6.06 (6.6)	*h* (10.5)	4.20	2.95	3.38	3.38	3.67, 3.81 (2 × OMe), 7.61—8.44 (4 H, m, ArH)	536
(**18c'**)[a]	5.18 (4.6)	6.09 (2.4)	3.79 (4.6)	*h*	3.10	3.33	3.48	3.67, 3.85 (2 × OMe), 7.58—8.30 (4 H, m, ArH)	536
(**18d**)[c]	5.22 (5.2)	5.62 (3.0)	3.71 (6.1)	3.77	3.11	3.24	3.44	2.10—2.43 (12 H, 4 × Me), 3.57, 3.82 (2 × OMe), 6.98 (1 H)	512
(**15a**)[a]	5.49 (6.3)	5.36 (6.9)	4.22 *h*	4.11	3.09	3.28	3.36	6.94—7.55 (10 H, m, Ph)	501
(**19a**)[a]	5.46 (5.2)	5.12 (5.8)	4.13 *h*	4.07	3.19	3.30	3.48	6.87—7.80 (10 H, m, Ph)	501
(**15b**)[a]	5.51 (7.4)	5.18 (7.1)	4.32 (10.5)	3.90	3.04	3.29	3.33	3.72 (OMe), 6.88—7.58 (10 H, m, Ph)	534
(**19b**)[a]	5.53 (3.8)	5.02 (5.2)	4.05 *h*	4.02	3.08	3.29	3.48	3.85 (OMe, 6.92—7.80 (10 H, m, Ph)	534
(**19c**)[e]	5.44 (3.3)	6.65 (0.0)	4.28 (0.0)	4.26	3.17	3.35	3.46	7.03—7.60 (15 H, m, Ph)	580
(**19d**)[e]	5.51 (3.7)	6.10 (6.0)	4.20 (0.0)	4.20	3.18	3.24	3.44	6.39 (1 H), 7.20—7.50 (10 H, m, Ph), 2.12—2.40 (12 H, m, 4 × Me)	636

[a–e] Spectrometers used were [a] 60, [b] 100, [c] 200, [d] 360, [e] 400 MHz machines. [f] The signals appeared at δ 4.8—5.3. [g] The signals appeared at δ 4.75—5.4. [h] *J*-Values could not be determined because of signal overlap.

electronegative groups on N-7 might make form 2A (*E*-ylide) unstable and cause the ylides to reside exclusively in the 2B form (*Z*-ylide).



(**2A**)
E-ylide



(**2B**)
Z-ylide

The results of the reactions were grouped into three cases depending on whether they gave Type-I, Type-II, or a mixture of Type-I and Type-II products (Table 3). When the ylides (**2a—c**) containing relatively small substituents (R = CN, CO_2Me, COPh) reacted with fumaronitrile (X = CN) or dibenzoylethylene (X = COPh), only Type-I products, (**12**) and (**13**), were obtained. Reactions of ylides (**2a—c**) with fumarates afforded mixtures of Types I and II, and exceptionally the reaction of diphenyl fumarate with compound (**2c**) afforded only Type-II product (**19c**) (86.2% yield). Similar results have been observed in the formation of pyrrolo[2,1-*a*]isoquinoline derivatives from the reaction of 3,4-dihydroisoquinolinium methylide with dimethyl fumarate.[7d] Secondary orbital interaction of dimethyl fumarate and the ylides is not so large that it cannot regulate a reaction path (path a or b in Scheme 2) and

Table 5. Solvent effects on the reaction of ylide (**2c**) with dimethyl fumarate

Solvent[a]	Reaction time	Product[b] (**14c**) Type I	Product[b] (**18c**) Type II
DMF	15 min	63	37
Acetone	1 h	64	36
CH_2Cl_2	3 h	59	41
Benzene	> 5 days	54	46
Diethyl ether	> 5 days	61	39
MeCN	30 min	59	41

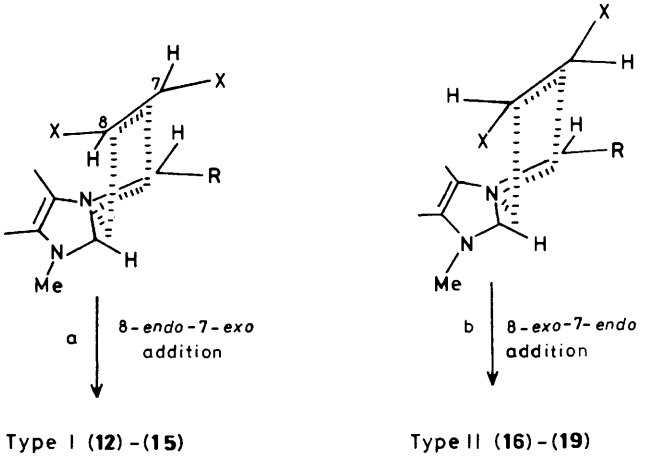
[a] Reaction temperature = room temperature. [b] Ratios were determined by the intensities of singlets due to the N(9)–Me groups in the ^{1}H n.m.r. spectrum of the reaction mixture.

Table 6. Thermal effects on the reaction of ylides (**2**) with *trans*-olefins

Temperature (°C)	Time	Product[a] (**14c**) Type I	Product[a] (**18c**) Type II	Product[b] (**12d**) Type I	Product[b] (**16d**) Type II
−40	1 h	66	34	75	25
Room temp.	30 min	59	41	67	33
81.6 (reflux)	20 min	52	48	58	42

[a] Obtained from the reaction of ylide (**2c**) with dimethyl fumarate. [b] Obtained from the reaction of ylide (**2d**) with fumaronitrile.

the steric effect of R in the ylides sensitively affects the selection of the reaction path. In contrast, Type-II products (**17d**), (**18d**), and (**19d**) were exclusively obtained from the bulky ylide (**2d**) *via* path b which contains the 8-*exo*-7-*endo* transition state. From these results, the stereoselectivity of xanthinium *N*(7)-methylides with *trans*-symmetric olefins was controlled by the balance of the secondary orbital interaction and steric repulsion.



Scheme 2. Numbering refers to that of the tricyclic product

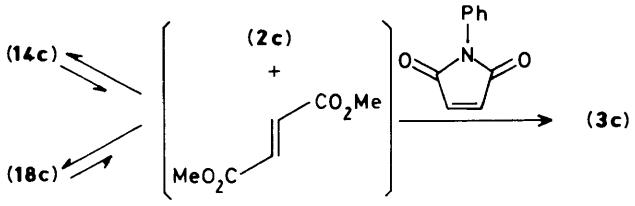
The effects of reaction temperature were then investigated (Table 6). The reaction of ylide (**2c**) with dimethyl fumarate at −40 °C afforded Type-I (**14c**) and -II (**18c**) products in the ratio 66:34, whilst at reflux (81.6 °C) the ratio was shifted to 52:48. Similar product ratios [Type I, (**12d**); Type II, (**16d**)] were obtained from the reaction of the bulky ylide (**2d**) and fumaronitrile. This result showed that Type I was the kinetically controlled product and that Type II was the thermodynamically controlled one.[7b] Indeed the reactions of less hindered ylides

Table 7. ^{1}H N.m.r. spectral data for compounds (**8**)—(**10**)[a]

Compd.	6-H	8a-H	9-Me	1-Me	3-Me	Others
(**8a**)	4.85	5.27	3.20	3.25	3.50	2.20—2.70 (m, CH_2)
(**8b**)	4.52	5.28	3.16	3.28	3.53	3.77 (OMe)
(**8c**)	5.80	5.12	3.15	3.47	3.65	7.48—7.70, 8.25—7.43 (5 H, m, Ph)
(**9a**)	4.69	5.32	3.04	3.28	3.41	3.80 (OMe)
(**9b**)	4.56	5.33	2.98	3.28	3.40	3.76, 3.78 (2 × OMe)
(**9c**)	5.74	5.19	2.94	3.33	3.37	3.72 (OMe), 7.35—7.65, 8.20—8.40, (5 H, m, Ph)
(**10a**)	4.68	5.31	3.06	3.28	3.42	1.32 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 4.27 (2 H, q, *J* 7.0 Hz, OCH_2)
(**10b**)	5.45	5.34	3.00	3.28	3.41	1.30 (3 H, t, *J* 7.5 Hz, CH_2*Me*), 3.78 (OMe), 4.37 (2 H, q, *J* 7.5 Hz, OCH_2)
(**10c**)	5.75	5.19	2.98	3.36	3.39	1.30 (3 H, t, *J* 7.4 Hz, CH_2*Me*), 4.42 (2 H, q, *J* 7.4 Hz, OCH_2), 7.47—7.65, 8.33—8.45 (5 H, m, Ph)

[a] 200 MHz for (**10c**) and 60 MHz for the others.

(**2a**—**c**) of which the 8-*endo* transition state might be stabilised by secondary orbital interaction gave Type-I adducts stereoselectively. The interconversion of the stereoisomers was not observed when the ylides were generated with Et_3N in MeCN at room temperature, followed by reaction with dipolarophiles. Hence, all the products were primary adducts *via* an independent reaction course (path a or b in Scheme 2).



Scheme 3.

The stabilities of the 1,3-dipolar cycloadducts have been investigated by several groups. The adducts were easily interconverted between stereoisomers *via* retro-reaction and recombination.[5,6] The possibility of interconversions between adducts (**14c**) and (**18c**) was examined. After compound (**14c**) had been refluxed in MeCN for 12 h, the appearance of its isomer (**18c**) was observed and the ratio (**14c**):(**18c**) was 9:1 from the ^{1}H n.m.r. spectrum. On the other hand, adduct (**14c**) was not detected when isomer (**18c**) was refluxed in MeCN for 12 h. When compound (**14c**) was refluxed in MeCN for 12 h with 1 mol equiv. of *N*-phenylmaleimide,[4b,5,6] a mixture of compounds (**14c**) and (**3c**) was obtained in the ratio 3:1. From these results we deduced that the 1,3-dipolar cycloaddition of ylides (**2a**—**d**) with olefins was indeed reversible, but that the retro-reaction process was not important at or below room temperature.

Experimental

M.p.s were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed at the Microanalytical Laboratory of our university. ^{1}H N.m.r.

Table 8. Physicochemical data for adducts (3), (8)—(10), and (12)—(19)

Compd.	M.p. (°C)	Appearance	Recryst. solvent	Formula	Found (%) (Required) C	H	N
(3a)	204—207[a]	Colourless prisms	MeCN	$C_{20}H_{18}N_6O_4$	58.95 (59.1)	4.4 (4.5)	20.7 (20.7)
(3b)	198—201[a]	Colourless prisms	MeOH	$C_{21}H_{21}N_5O_6 \cdot 0.5H_2O$	56.6 (56.25)	5.0 (4.9)	15.7 (15.6)
(3c)	202—204[a]	Orange prisms	MeCN	$C_{26}H_{23}N_5O_5$	64.6 (64.3)	4.8 (4.8)	14.55 (14.4)
(8a)	215—216	Colourless prisms	AcOEt	$C_{13}H_{14}N_6O_2$	54.5 (54.5)	4.9 (4.9)	29.5 (29.35)
(8b)	165—167	Colourless prisms	CH_2Cl_2–hex[c]	$C_{14}H_{17}N_4O_4$	52.4 (52.7)	5.3 (5.4)	21.9 (21.9)
(8c)	164—165[b]	Yellow prisms	AcOEt–hex[c]	$C_{19}H_{19}N_5O_3 \cdot 0.25AcOEt$	61.8 (62.0)	5.5 (5.45)	18.3 (18.1)
(9a)	182—184	Colourless prisms	AcOEt	$C_{14}H_{17}N_5O_4$	52.5 (52.7)	5.4 (5.4)	21.8 (21.9)
(9b)	141—143	Colourless prisms	AcOEt	$C_{15}H_{20}N_4O_6 \cdot 0.25AcOEt$	51.3 (51.3)	6.0 (5.9)	14.9 (15.0)
(9c)	162—162.5	Yellow needles	AcOEt	$C_{20}H_{22}N_4O_5$	60.1 (60.3)	5.6 (5.6)	14.0 (14.1)
(10a)	198—201[a]	Colourless needles	AcOEt	$C_{15}H_{19}N_5O_4$	53.8 (54.05)	5.7 (5.75)	20.9 (21.0)
(10b)	152—155	Colourless prisms	MeOH	$C_{16}H_{22}N_4O_6$	52.4 (52.45)	6.0 (6.05)	15.2 (15.3)
(10c)	162—164	Yellow needles	EtOH	$C_{21}H_{24}N_4O_5$	61.4 (61.2)	5.9 (5.9)	13.6 (13.6)
(12a)	181.5—183.5[a]	Colourless prisms	MeCN	$C_{14}H_{13}N_7O_2$	54.1 (54.0)	4.2 (4.2)	31.6 (31.5)
(12b)	189—191	Colourless prisms	$CHCl_3$	$C_{15}H_{16}N_6O_4$	52.2 (52.3)	4.6 (4.7)	24.5 (24.4)
(12c)	163—166	Yellow needles	MeCN	$C_{20}H_{18}N_6O_3$	61.35 (61.5)	4.6 (4.65)	21.3 (2.15)
(12d)	175—178[a]	Colourless prisms	AcOEt–Et_2O	$C_{24}H_{26}N_6O_3$	64.3 (64.6)	5.9 (5.8)	18.7 (18.8)
(13a)	188—190[a]	Yellow prisms	AcOEt	$C_{26}H_{23}N_5O_4$	66.4 (66.5)	5.0 (4.9)	14.9 (14.9)
(13b)	175—176	Yellow prisms	ACOEt	$C_{27}H_{26}N_4O_6$	64.25 (64.5)	5.2 (5.2)	11.1 (11.15)
(13c)	168—170	Yellow prisms	AcOEt	$C_{32}H_{28}N_4O_5$	69.8 (70.1)	5.1 (5.1)	10.05 (10.2)
(14a)	165.5—167	Colourless prisms	AcOEt	$C_{16}H_{19}N_5O_6$	50.9 (40.9)	5.1 (5.1)	18.7 (18.6)
(14b)	164—165	Colourless prisms	AcOEt	$C_{17}H_{22}N_4O_8$	49.65 (49.75)	5.45 (5.4)	13.6 (13.65)
(14c)	136—138	Yellow prisms	AcOEt	$C_{22}H_{24}N_4O_7$	57.35 (57.9)	5.3 (5.3)	12.2 (12.3)
(14c′)	190—192[a]	Yellow needles	AcOEt	$C_{22}H_{23}BrN_4O_7$	49.2 (49.4)	4.3 (4.3)	10.5 (10.5)
(15a)	192—195[a]	Colourless needles	AcOEt	$C_{26}H_{23}N_5O_6$	62.0 (62.3)	4.7 (4.6)	13.9 (14.0)
(15b)	184—188[a]	Colourless prisms	MeOH	$C_{27}H_{26}N_4O_8$	60.55 (60.7)	5.0 (4.9)	10.5 (10.5)
(16d)	198—199[a]	Colourless needles	AcOEt	$C_{24}H_{26}N_6O_3$	64.3 (64.6)	5.9 (5.8)	19.65 (18.8)
(17d)	235—237[a]	Colourless prisms	AcOEt	$C_{36}H_{36}N_4O_5$	71.3 (71.5)	6.1 (6.0)	8.9 (6.3)
(18a)	172—173	Colourless prisms	AcOEt	$C_{16}H_{19}N_5O_6$	51.0 (50.9)	5.1 (5.1)	18.6 (18.6)
(18b)	151—152	Colourless prisms	AcOEt	$C_{17}H_{22}N_4O_8$	49.6 (49.75)	5.5 (5.4)	13.6 (13.65)
(18c)	191—193[a]	Yellow prisms	AcOEt	$C_{22}H_{24}N_4O_7$	57.9 (57.9)	5.3 (5.3)	12.3 (12.3)
(18c′)	175—176[a]	Yellow needles	AcOEt	$C_{22}H_{23}BrN_4O_7$	49.25 (49.4)	4.3 (4.3)	10.5 (10.5)
(18d)	195—197[a]	Colourless needles	AcOEt	$C_{26}H_{32}N_4O_7$	60.7 (60.9)	6.3 (6.3)	11.0 (10.9)
(19a)	85—87	Colourless needles	AcOEt	$C_{26}H_{23}N_5O_6$	62.2 (62.3)	4.6 (4.6)	14.1 (14.0)

Table 8 (*continued*)

Compd.	M.p. (°C)	Appearance	Recryst. solvent	Formula	Found (%) (Required) C	H	N
(**19b**)	86—89	Colourless prisms	MeOH	$C_{27}H_{26}N_4O_8$	60.4 (60.7)	4.9 (4.9)	10.4 (10.5)
(**19c**)	180—182[a]	Yellow needles	AcOEt	$C_{36}H_{28}N_4O_7$	66.3 (66.2)	4.8 (4.9)	9.6 (9.65)
(**19d**)	163—165[a]	Colourless needles	MeOH	$C_{36}H_{36}N_4O_7$	67.9 (67.9)	5.7 (5.7)	8.9 (8.8)

[a] M.p. with decomposition. [b] First m.p. 111—114 °C. [c] Hex = n-hexane.

spectra were recorded on Bruker WH-400 (400 MHz), Nicolet QE-360 (360 MHz), JEOL FX-200 (200 MHz), and Hitachi R-20B (60 MHz) spectrometers (Tables 1, 2, 4, and 7) with tetramethylsilane as an internal standard. I.r. spectra were determined on a JASCO Model IRA-1 spectrometer. Electron-impact mass spectra were determined on a JEOL D-300 machine.

Synthesis of 7-(4-*Bromophenacyl*)-1,3,9-*trimethylxanthinium Toluene*-p-*sulphonate* (**1c'**).—To a solution of theophylline (1,3-dimethylxanthine) (1.8 g, 10 mmol) in *N*,*N*-dimethylformamide (DMF) (10 ml) was added 60% (w/w) NaH (0.4 g, 10 mmol) and the mixture was stirred for 30 min at 0 °C. 4-Bromophenacyl bromide (2.78 g, 10 mmol) was added and the reaction mixture was stirred for 5 h at room temperature. After removal of DMF under reduced pressure, water was added to the residue and the mixture was extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and evaporated to give crude 7-(4-bromophenacyl)-theophylline (3.37 g, 89.3%) as a powder. Recrystallisation from EtOH gave *needles*, m.p. 201—203 °C (Found: C, 47.8; H, 3.4; N, 15.0. $C_{15}H_{13}BrN_4O_3$ requires C, 47.8; H, 3.5; N, 14.85%).

A mixture of 7-(4-bromophenacyl)theophylline (1 g) and methyl toluene-*p*-sulphonate (7 g) was heated at 140—160 °C for 2 h. After having cooled, the mixture was added to ether (100 ml) and the precipitated crystalline solid was collected. Recrystallisation from EtOH gave the *title product* as needles (1.36 g, 91.3%), m.p. 151—153 °C (Found: C, 49.05; H, 4.4; N, 9.6. $C_{23}H_{23}BrN_4O_6S$ requires C, 49.0; H, 4.1; N, 9.9%).

Synthesis of 1,3,9-*Trimethyl*-7-(2,3,5,6-*tetramethylphenacyl*)-*xanthinium Toluene*-p-*sulphonate* (**1d**).—7-(2,3,5,6-Tetramethylphenacyl)theophylline was synthesised from theophylline (9 g, 0.05 mol) and 2,3,5,6-tetramethylphenacyl bromide (19.1 g, 0.075 mol) [prepared from 2,3,5,6-tetramethylacetophenone[14] and $CuBr_2$ (2 mol equiv.) in CH_2Cl_2] in a similar way to that described above. Recrystallisation from EtOH afforded *needles* for 7-(4-bromophenacyl)theophilline (9.32 g, 82.4%), m.p. 235—236.5 °C (decomp.) (Found: C, 64.1; H, 6.2; N, 15.7. $C_{19}H_{22}N_4O_3$ requires C, 64.4; H, 6.3: N, 15.8%).

A mixture of the theophylline (12.5 g) and methyl toluene-*p*-sulphonate (50 ml) was heated at 140—160 °C for 2.5 h. After having cooled, the mixture was poured into ether and the precipitated oil was separated. The oil was crystallised from EtOH to give the *title compound* (**1d**)(16.0 g, 84.6%) as needles, m.p. 253—255 °C (Found: C, 59.9; H, 6.1; N, 10.45. $C_{27}H_{32}N_4O_6S$ requires C, 60.0; H, 6.0; N, 10.4%).

General Procedure for the Reactions of Xanthinium N(7)-*Methylides* (**2**) *with Olefinic Dipolarophiles.*—Et_3N (0.14 ml) was added to a stirred suspension of the toluenesulphonate (**1**) (1 mmol) and olefinic dipolarophile (1.1 mmol) in dry MeCN (10 ml), and the mixture was stirred at room temperature for 0.5—2 h. After the solvent had been evaporated off under reduced pressure, the residue was extracted with CH_2Cl_2, dried ($MgSO_4$), and evaporated under reduced pressure. The crude products were purified by recrystallisation from appropriate solvents (Table 8) or separated by silica-gel column chromatography with a mixture of AcOEt and n-hexane as eluant to give the adducts (**3**), (**8**)—(**10**), and (**12**)—(**19**). Reactions of the ylides (**2**) with *cis*-olefins afforded the uracil derivatives (**7**) which were identical with the hydrolysis products of compounds (**2**).[8]

Dehydrogenation of Compound (**10c**).—Crude compound (**10c**) obtained from the tosyl derivative (**1c**) (969 mg, 2 mmol) and ethyl acrylate was treated with a solution of chloranil (502 mg) in benzene (30 ml). The solution was concentrated and the residual crude oil was chromatographed on silica gel with AcOEt–n-hexane (1:1) as eluant. Ethyl 6-benzoyl-1,3,9-trimethyl-2,4-dioxo-2,3,4,9-tetrahydro-1*H*-pyrrolo[2,1-*f*]-purine-8-carboxylate (**11**) (409 mg, 50%) was obtained by recrystallisation from EtOH as *prisms*, m.p. 282—283 °C (Found: C, 61.4; H, 5.0; N, 13.7. $C_{21}H_{20}N_4O_5$ requires C, 61.8; H, 4.9; N, 13.7%); δ (60 MHz; $CDCl_3$) 1.37 (3 H, t, *J* 7.5 Hz, CH_2Me), 3.45, 3.85, and 4.45 (each s, 3 × NMe), 4.25 (2 H, q, *J* 7.5 Hz, CH_2), 7.25 (1 H, s, 7-H), and 7.40—7.75 and 7.95—8.15 (5 H, m, Ph).

Reaction of Ylide (**2b**) *with Dimethyl Maleate.*—n-Butyllithium (1.0M; 1.1 ml) was slowly added to a stirred suspension of compound (**1b**) (0.439 g, 1 mmol) in dry THF (40 ml) at −70 °C under nitrogen, and the mixture was stirred for 15 min. A solution of dimethyl maleate (159 mg, 1.1 mmol) in dry THF (10 ml) was slowly added to the pale yellow solution, and the temperature was raised to −10 °C for 2 h. The reaction mixture was then treated with saturated aq. NH_4Cl and extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and evaporated to give a yellow oil, which was purified by column chromatography with AcOEt–n-hexane as eluant to give a crystalline solid. Recrystallisation from CH_2Cl_2 afforded *dimethyl* (3R*,3aR*)-5,6,8-*trimethyl*-4,7,9-*trioxo*-3,3a,4,5,6,7,8,9-*octahydropyrrolo*-[1,2-f]*pteridine*-2,3-*dicarboxylate* (**6**) (118 mg, 49.7%) as prisms, m.p. 174—176 °C (Found: C, 50.3; H, 4.8; N, 14.7. $C_{16}H_{18}N_4O_7$ requires C, 50.8; H, 4.8; N, 14.8%); δ (60 MHz; $CDCl_3$) 3.25, 3.32, and 3.40 (3 × NMe), 3.65 and 3.72 (2 × OMe), 4.60 (1 H, dd, *J* 5.7 and 1.5 Hz, 3-H), 4.63 (1 H, d, *J* 5.7 Hz, 3a-H), and 7.62 (1 H, d, *J* 1.5 Hz, 1-H); *m/z* 378 (M^+).

Retro-Diels–Alder Reaction of Diesters (**14c**) *and* (**18c**).—(*Ex. A*). A solution of diester (**14c**) and 1 mol equiv. of *N*-phenylmaleimide in MeCN was refluxed for 12 h and the solvent was then evaporated off. The crude product was analysed by ^1H n.m.r. spectroscopy and was seen to be a mixture of compounds (**14c**) and (**3c**) in the ratio 3:1.

(*Ex. B*). The reaction of compound (**18c**) and *N*-phenylmaleimide under similar conditions led to a 9:1 mixture of compounds (**18c**):(**3c**).

Table 9. Atomic co-ordinates (× 10^4) (standard deviations in parentheses)

	x		*y*		*z*	
Atom	A	B	A	B	A	B
Br	4 214(1)	1 290(1)	7 496(1)	−766(0)	5 286(3)	5 537(2)
C(1)	5 485(6)	2 659(6)	4 670(4)	1 976(4)	5 546(19)	4 575(17)
C(2)	4 530(6)	1 719(7)	4 265(5)	2 361(4)	5 874(16)	5 206(16)
C(3)	4 343(6)	1 532(6)	4 681(4)	1 953(4)	5 345(16)	4 730(17)
C(4)	3 673(6)	854(6)	4 786(5)	1 840(5)	4 931(19)	4 712(18)
C(5)	3 422(7)	615(7)	3 982(4)	2 630(5)	5 742(21)	5 563(18)
C(6)	2 525(7)	−308(7)	4 487(6)	2 075(6)	4 778(26)	5 241(24)
C(7)	4 306(9)	1 519(8)	3 455(5)	3 191(4)	6 553(23)	5 799(22)
C(8)	5 440(8)	2 733(8)	4 098(6)	2 583(5)	7 959(21)	6 896(19)
C(9)	4 979(6)	2 092(6)	5 223(4)	1 420(4)	3 606(16)	2 803(151)
C(10)	5 359(5)	2 429(6)	4 882(4)	1 749(4)	2 447(16)	1 545(16)
C(11)	5 824(6)	2 935(6)	4 639(4)	2 003(4)	3 691(17)	2 641(16)
C(12)	5 969(6)	3 012(7)	4 154(4)	2 500(4)	3 251(18)	2 065(16)
C(13)	6 718(10)	3 737(10)	3 558(5)	3 116(5)	3 887(27)	1 998(26)
C(14)	5 689(6)	2 751(7)	5 106(4)	1 525(4)	927(17)	−52(16)
C(15)	5 596(8)	2 625(8)	5 705(5)	905(5)	−1 153(21)	−2 024(17)
C(16)	5 395(6)	2 512(5)	5 637(4)	998(4)	3 991(18)	3 114(15)
C(17)	5 073(6)	2 196(6)	6 066(4)	581(4)	4 310(17)	3 658(17)
C(18)	4 412(6)	2 590(6)	6 151(4)	218(5)	3 945(21)	3 921(21)
C(19)	4 157(6)	2 342(7)	6 578(5)	−196(5)	4 184(19)	4 480(21)
C(20)	4 577(7)	1 651(7)	6 919(5)	−218(4)	4 844(18)	4 759(18)
C(21)	5 233(8)	1 247(6)	6 840(4)	139(4)	5 252(23)	4 448(21)
C(22)	5 478(7)	1 513(6)	6 413(4)	543(4)	4 956(22)	3 902(20)
O(1)	3 462(4)	623(4)	5 154(3)	1 455(3)	4 448(14)	4 346(14)
O(2)	3 022(5)	227(5)	3 682(4)	2 925(4)	5 904(18)	5 883(16)
O(3)	5 678(6)	2 614(5)	3 920(3)	2 696(3)	2 248(16)	1 269(14)
O(4)	6 497(4)	3 596(4)	4 020(3)	2 650(3)	4 169(14)	2 582(14)
O(5)	6 204(5)	3 236(5)	4 983(3)	1 645(3)	250(15)	−806(14)
O(6)	5 332(4)	2 385(4)	5 445(3)	1 170(3)	337(12)	−561(12)
O(7)	5 993(4)	3 109(4)	5 595(3)	1 024(3)	4 062(14)	2 947(12)
N(1)	5 204(5)	2 411(5)	4 243(4)	2 409(3)	6 184(14)	5 293(13)
N(2)	4 887(5)	2 076(5)	4 980(3)	1 661(3)	5 332(14)	4 512(14)
N(3)	4 096(5)	1 296(5)	3 915(3)	2 711(3)	6 079(15)	5 557(13)
N(4)	3 250(5)	421(5)	4 417(4)	2 190(4)	5 202(16)	5 191(5)

(*Ex. C*). A solution of compound (**14c**) in MeCN was refluxed for 12 h and the solvent was then evaporated off. The residual mass was analysed by ^{1}H n.m.r. spectroscopy and was seen to be a mixture of compounds (**14c**) and (**18c**) in the ratio 9:1. Under the same reaction conditions compound (**14c**) was not detected when compound (**18c**) was refluxed in MeCN.

X-*Ray Molecular Structure Determination of Compound* (**14c'**).—*Data collection and processing.* A crystal with the approximate dimensions of 0.2 × 0.3 × 0.4 mm was used for the intensity measurements. The density was determined by the flotation method in a mixture of light petroleum and carbon tetrachloride. The cell constants were determined by the least-squares procedure from the 20 values of 24 reflections measured on a diffractometer using monochromated Cu-K_α radiation. Three-dimensional intensity data were collected on a Rigaku automatic four-circle diffractometer with graphite-monochromated Cu-K_α radiation. Background was counted for 5 s at both sides of each peak. Three standard reflections were measured every 50 reflections during the course of collection. A total of 4 604 independent reflections was collected. Reflections having an intensity exceeding the corresponding standard deviations by a factor of three were treated as observed. 3 445 Reflections were retained and corrected for Lorentz and polarisation factors but not for absorption.

Crystal data for compound (**14c'**). $C_{22}H_{23}BrN_4O_7$, M = 535.353. Orthorhombic, a = 20.226(2), b = 29.949(3), c = 7.611(1) Å, V = 4 610.0(8) Å^3. Space group $Pn2_1a$, Z = 8, D_x = 1.543 g cm^{-3}.

Structure analysis and refinement. The structure was determined by the heavy-atom method. From the three-dimensional Patterson map, the position of one bromine atom was easily deduced. From the Fourier synthesis with the phases, another bromine atom was obtained. All the non-hydrogen atoms in the asymmetric unit were obtained from the Fourier map phases by reference to the two bromine atoms. The oxygen and nitrogen atoms were identified from structural considerations. Refinement of atomic parameters was carried out by the full-matrix least-squares method, the quantity minimised being $\Sigma w(|F_o| - |F_c|)^2$, with w = 1.0 for all the reflections used. From the difference map, all the hydrogen atoms, except the hydrogen atoms of methyl groups, were obtained. The final R-value was 0.069. The atomic scattering factors for C, O, N were given by Cromer and Mann,[15] that for H by Stewart *et al.*,[16] and that for Br from International Tables for X-ray Crystallography.[17] The final atomic co-ordinates for non-hydrogen atoms of the racemate (A and B) are given in Table 9.*

* Supplementary data (see section 5.6.3 of Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1987, issue 1). Tables of anisotropic thermal parameters of the non-hydrogen atoms, isotropic temperature factors for hydrogen atoms, and bond lengths, bond angles, and torsion angles have been deposited at the Cambridge Crystallographic Data centre.

Acknowledgements

We express our gratitude to Miss R. Tanaka and Mr. Y. Usami for their technical assistance.

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Received 3*rd March* 1986; *Paper* 6/420