An Unexpected Double Cycloaddition of [1,2,4]Triazolo[1,5-*a*]pyrimidine *N*-Ylide with Activated Acetylenes and Alkenes

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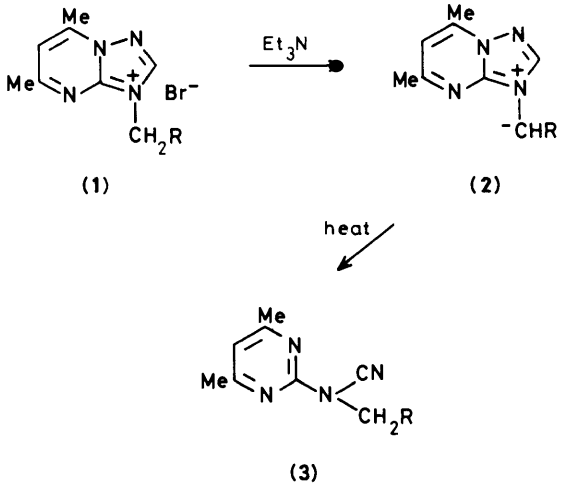
The reaction of 5,7-dimethyl-[1,2,4]triazolo[1,5-*a*]pyrimidinio-3-phenacylide (**5**) with activated acetylenes gave 1:2 adducts of ylide–R–C≡C–R. The structures of the products were determined as 3,3a-dihydropyrazolo[1,5-*c*]pyrimidine derivatives (**7**) by hydrolysis, ^{1}H and ^{13}C n.m.r., and *X*-ray crystallography. Molecular orbital calculations (*ab initio*) of the model compounds were performed in order to elucidate the mechanism for the formation of the 1:2 adducts. The results of the calculations suggested that an intermediate, 1:1 adduct would be less reactive than the starting ylide. However, despite many attempts isolation of the 1:1 adduct was unsuccessful. The 1:2 adduct was obtained even from the reaction of the ylide with 0.5 equiv. of the acetylenic compound. Easy formation of the 1:2 adducts can be explained by an equilibrium between the 1:1 adducts and the starting materials.

Recently, we reported the generation and thermal reaction of 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinio-3-methylides (**2**). Ylides (**2**) generated *in situ* from the iminium salts (**1**) and triethylamine (1 equiv.) easily underwent a thermal reaction in refluxing acetonitrile to give the pyrimidine derivatives (**3**) (Scheme 1).[1]



Scheme 1.

Since, at 0 °C, the thermal reaction is slow we conducted the reaction of [1,2,4]triazolo[1,5-*a*]pyrimidinio-3-phenacylide (**5**) with activated acetylenes at this temperature. In this paper, we describe the structure determination of the products and a plausible reaction mechanism for the double cycloaddition of the ylide (**5**) with activated acetylenes.[2]

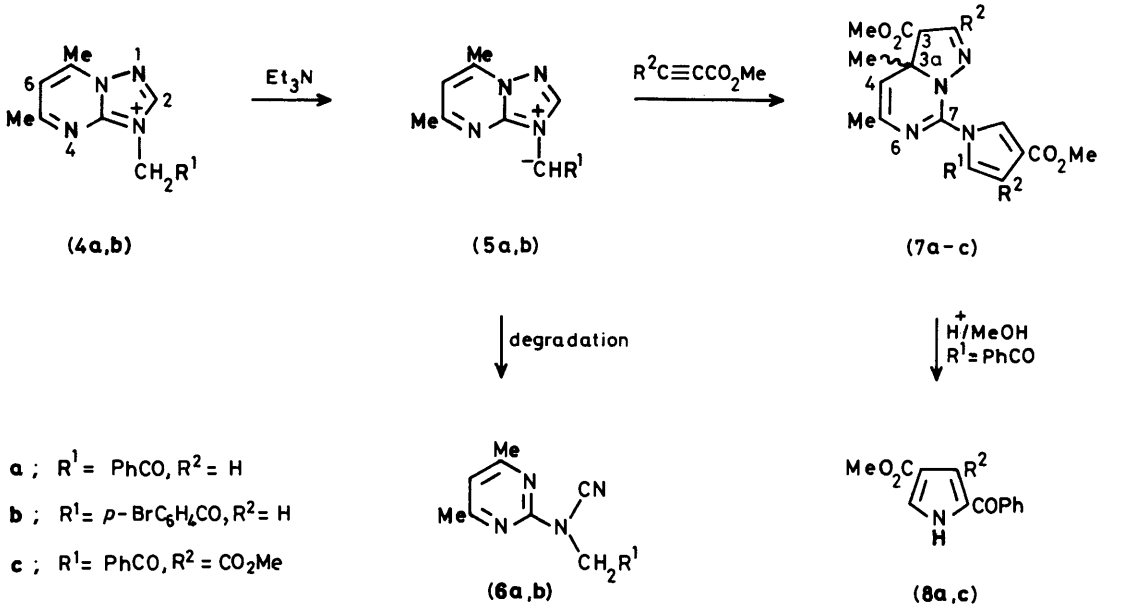
Results and Discussion

Reaction of 5,7-*Dimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinio*-3-*phenacylide with Methyl Propiolate* (*MP*) *or Dimethyl Acetylenedicarboxylate* (*DMAD*).—5,7-Dimethyl-3-phenacyl[1,2,4]triazolo[1,5-*a*]pyrimidinium bromide (**4a**) was treated with triethylamine (1.1 equiv.) in the presence of MP (1.5 equiv.) at 0 °C to give two products, one of which was the pyrimidine derivative (**6a**) (18.5%), identical with an authentic sample of the thermal reaction product of the ylide (**5a**). The other product (**7a**) (26.5%) was determined to be the 1:2 adduct of (**5a**)–MP by mass spectroscopy and elemental analysis. Hydrolysis of compound (**7a**) under acidic conditions gave the pyrrole derivative (**8a**) (Scheme 2).

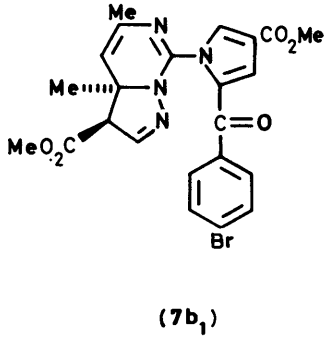
On the other hand, the ^{1}H n.m.r. spectra of (**7a**) showed four singlets due to Me groups at 1.16—1.96 p.p.m., and four singlets assigned to the Me groups of CO_2Me at 3.72—3.82 p.p.m. These signals indicated that compound (**7a**) is composed of two diastereoisomers (5:4 ratio). The major isomer (**7a**$_1$) could be isolated by fractional recrystallisation from diethyl ether.

In the ^{1}H n.m.r. spectrum of the compound (**7a**$_1$), both the C(5)–Me and C(7)–Me protons of the starting material (**4a**) (see Scheme 2 for numbering) showed high field shifts at 1.96 and 1.37 p.p.m. The signal due to Me protons at 1.96 p.p.m. showed an allylic coupling (*J* 1.4 Hz) with a proton at 5.13 p.p.m. The marked high field shift of another signal due to Me protons at 1.37 p.p.m. suggested that C(7) of the starting material (**4a**) was changed from an unsaturated carbon to a saturated one in the reaction process. The ^{13}C n.m.r. spectrum of (**7a**$_1$) showed an absorption due to the Me carbon bound to an sp^3 carbon at 22.3 p.p.m. and an absorption due to the sp^3 carbon (quaternary carbon) at 63.8 p.p.m. These results and spin-decoupling techniques revealed the structure of (**7a**$_1$) to be 3,3a-dihydropyrazolo[1,5-*c*]pyrimidine derivative. Moreover, when the C(3a)–Me protons at 1.37 p.p.m. were irradiated, 20% of nuclear Overhauser effect (n.O.e.) was observed on the proton at 3.65 p.p.m. due to C(3)–H. This suggested that C(3a)–Me and C(3)–CO_2Me groups of (**7a**$_1$) adopt a *trans* configuration to each other (Scheme 5).

The reaction of 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinio-3-*p*-bromophenacylide (**5b**) with MP gave a pyrimidine derivative (**6b**) (6%) and a 1:2 adduct (**7b**) (21.5%) as a mixture of diastereoisomers (5:4 ratio). The major isomer (**7b**$_1$) could



Scheme 2.



(7b$_1$)

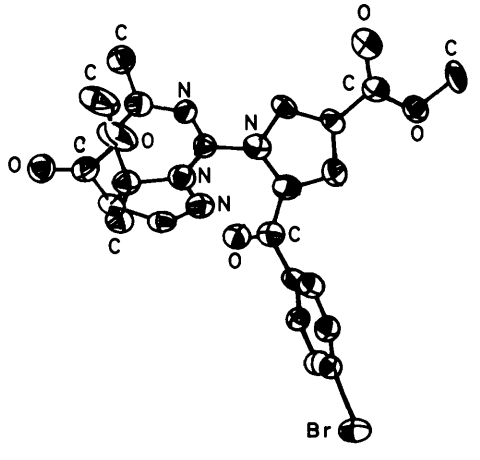


Figure 1. ORTEP drawing of (7b$_1$)

also be purified by fractional recrystallisation from diethyl ether, and its *X*-ray crystallography (Figure 1) supported the above structure elucidation for (7a$_1$). Moreover, DMAD reacted with 5,7-dimethyl-[1,2,4]triazolo[1,5-*a*]pyrimidinio-3-phenacylide (**5a**) in a similar manner to give the pyrimidine derivative (**6a**) (trace) and a 1:2 adduct (**7c**) as a mixture of diastereoisomers (5:1 ratio). The major isomer (**7c**$_1$) was isolated as above.

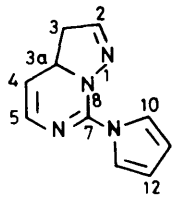
In these reactions, the minor isomers [(**7a**$_2$), (**7b**$_2$), (**7c**$_2$)] could not be isolated as pure forms from the mixtures of diastereoisomers (**7a**), (**7b**), and (**7c**) respectively. However, proton signals of the minor isomers in ^{1}H n.m.r. could be deduced from each mixture (Table 1) and were found to be close to the corresponding major isomers. As expected, the chemical shifts of the protons or Me protons at C(2), C(3), C(3a), and C(4) of the minor isomers were different from those of the corresponding major isomers by +0.4—−0.2 p.p.m.

Reaction of [1,2,4]*Triazolo*[1,5-a]*pyrimidinio-3-phenacylide with DMAD.*—The reaction of compound (**10**) with DMAD yielded a new cycloadduct (**12**) in 28% yield. The product (**12**) has a smaller molecular weight by 2 a.m.u. than that of the 1:2 adduct on the basis of mass spectral data.

Comparison of the ^{1}H n.m.r. spectra of (**12**) with that of (**7c**), showed that C(3)–H on the pyrazole ring of (**7c**$_1$) at 3.79 p.p.m. had disappeared. Moreover, C(4)–H of (**7c**$_1$) at 5.16 p.p.m. showed a marked downfield shift to 8.04 p.p.m. in compound (**12**), which coupled with an olefinic proton at 8.13 p.p.m. (*J* 5.9 Hz). These results suggested that compound (**12**) is a dehydrogenated compound of the 1:2 adduct (**11**) at C(3) and C(3a). The 10π aromatic stabilisation would accelerate the dehydrogenation.

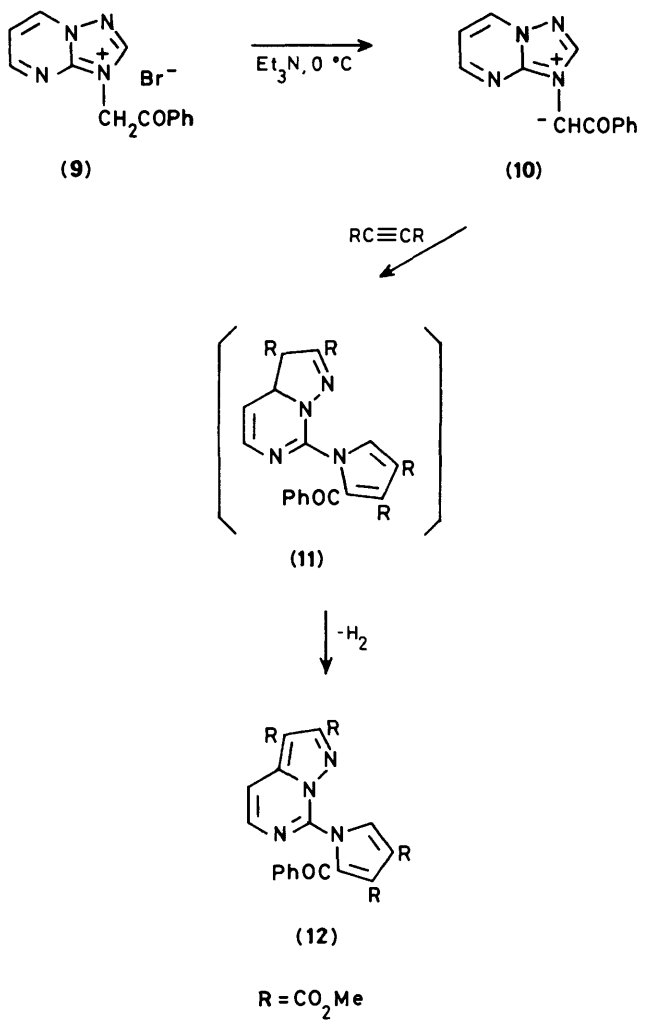
Reaction of 5,7-*Dimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinio*-3-p-*bromophenacylide with Alkenes.*—In contrast to the activated acetylenes, the reaction of triazolopyrimidinium ylides with most of the activated alkenes were unsuccessful (due to the formation of too many minor products to be isolated). However, the reaction of ylide (**5b**) with diphenylcyclopropenone and dimethyl fumarate (or dimethyl maleate) gave isolable products. The reaction of ylide (**5b**) with diphenylcyclopropenone proceeding *via* cleavage of the ylidic N–C bond gave two known compounds. One was 5,7-dimethyl[1,2,4]triazolo-[1,5-*a*]pyrimidine[3] (**16**) (74.5%) and the other was 6-(4-bromophenyl)-3,4-diphenyl-2*H*-pyran-2-one[4] (**15**) (62.5%). Reaction with dimethyl fumarate (or dimethyl maleate), however, gave a 1:1 adduct (**14**). The i.r. spectrum of compound (**14**) showed a

Table 1. ^{1}H n.m.r. spectra of 1:2 adduct[a] (7)



	C(3a)-Me	3-H	4-H	2-H	C(5)-Me	12-H	10-H	ArH	CO_2Me
(**7a**$_1$)[b]	1.37s	3.65d[c]	5.13q[d]	6.56d[c]	1.96d[d]	7.12d[e]	7.98d[e]	7.89—7.47m	3.82s, 3.72s
(**7b**$_1$)[f]	1.35s	3.65d[g]	5.16q[g]	6.58d[g]	1.93d[g]	7.10d[g]	8.00d[g]	7.88—7.50m	3.80s, 3.68s
(**7c**$_1$)[h]	1.32s	3.79s	5.16q[i]	—	1.93d[i]	—	7.95(s)	7.92—7.93m	3.83s, 3.70s[j], 3.26s
(**7a**$_2$)[k]	1.16s	4.10d[c]	5.43q[d]	6.75d[c]	1.93d[d]	7.12d[e]	7.93d[e]	7.89—7.47m	3.80s, 3.73s
(**7b**$_2$)[l]	1.15s	4.10d[g]	5.43q[g]	6.73d[g]	1.90d[g]	7.10d[g]	7.93d[g]	7.88—7.50m	3.80s, 3.75s
(**7c**$_2$)[m]	1.13s	4.10s	5.41q[i]	—	1.93d[i]	—	7.90s	7.92—7.33m	3.75s, 3.72s[j], 3.32s

[a] All spectra were run in $CDCl_3$. Chemical shift (δ) in p.p.m. [b] 400 MHz. [c] $J_{2,3}$ 1.4 Hz. [d] $J_{4,5\text{-Me}}$ 1.4 Hz. [e] $J_{10,12}$ 1.9 Hz. [f] 60 MHz. [g] Observed but not measurable. [h] 100 MHz. [i] $J_{4,5\text{-Me}}$ 1.3 Hz. [j] 6 H intensity was integrated. [k] Assigned from the ^{1}H n.m.r. (400 MHz and 100 MHz) of (**7a**$_1$) + (**7a**$_2$). [l] Assigned from the ^{1}H n.m.r. (60 MHz) of (**7b**$_1$) + (**7b**$_2$). [m] Assigned from the ^{1}H n.m.r. (100 MHz) of (**7c**$_1$) + (**7c**$_2$).



Scheme 3.

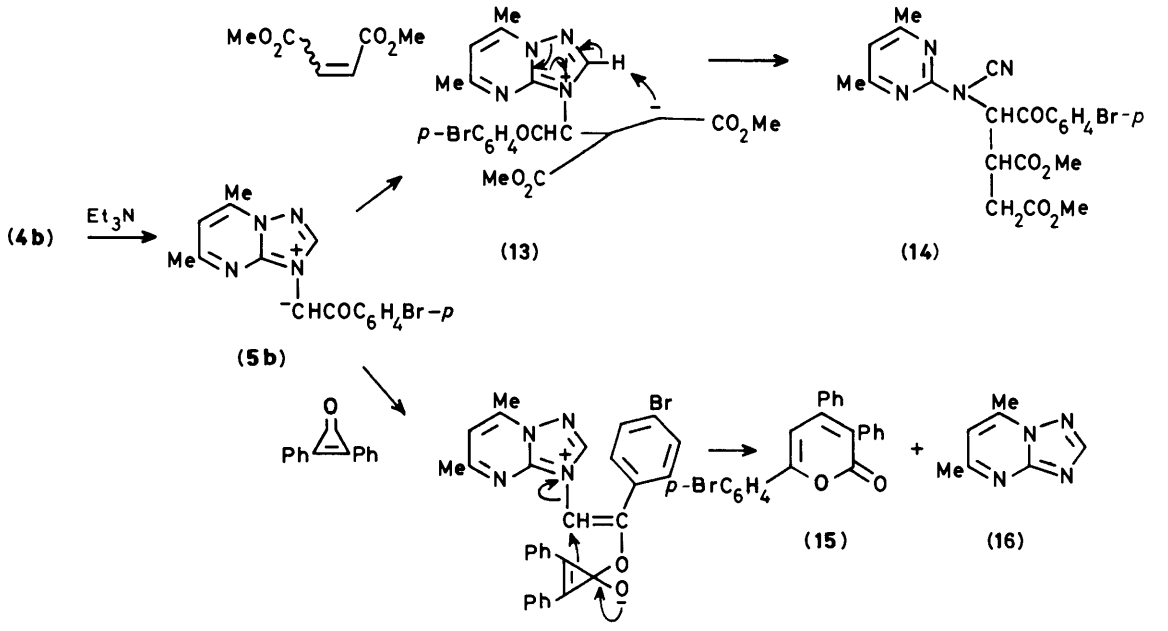
strong band for nitrile at 2 240 cm^{-1}. The ^{1}H n.m.r. spectrum exhibited a singlet at 2.4 p.p.m. for two Me groups of the pyrimidine ring and two pairs of the ester Me groups at 3.66, 3.65 and 3.63, 3.62 p.p.m. These facts suggested that compound (**14**) is a diastereoisomeric mixture of succinate derivatives (7:3 ratio). Moreover, spin-decoupling techniques revealed the existence of a 2,3-bis(methoxycarbonyl)-1-(4-bromobenzoyl)-propyl group.

Mechanism for the Formation of the 1:2 *Adducts.*—The reaction of triazolopyrimidinium ylides (**5**) with active acetylenes gave the 1:2 adducts (**7**). The 1:2 adduct (**7c**) was obtained even when DMAD (0.5 equiv.) was used. The 1:1 adducts were not isolated from the reaction of triazolopyrimidinium ylides with activated acetylenes.

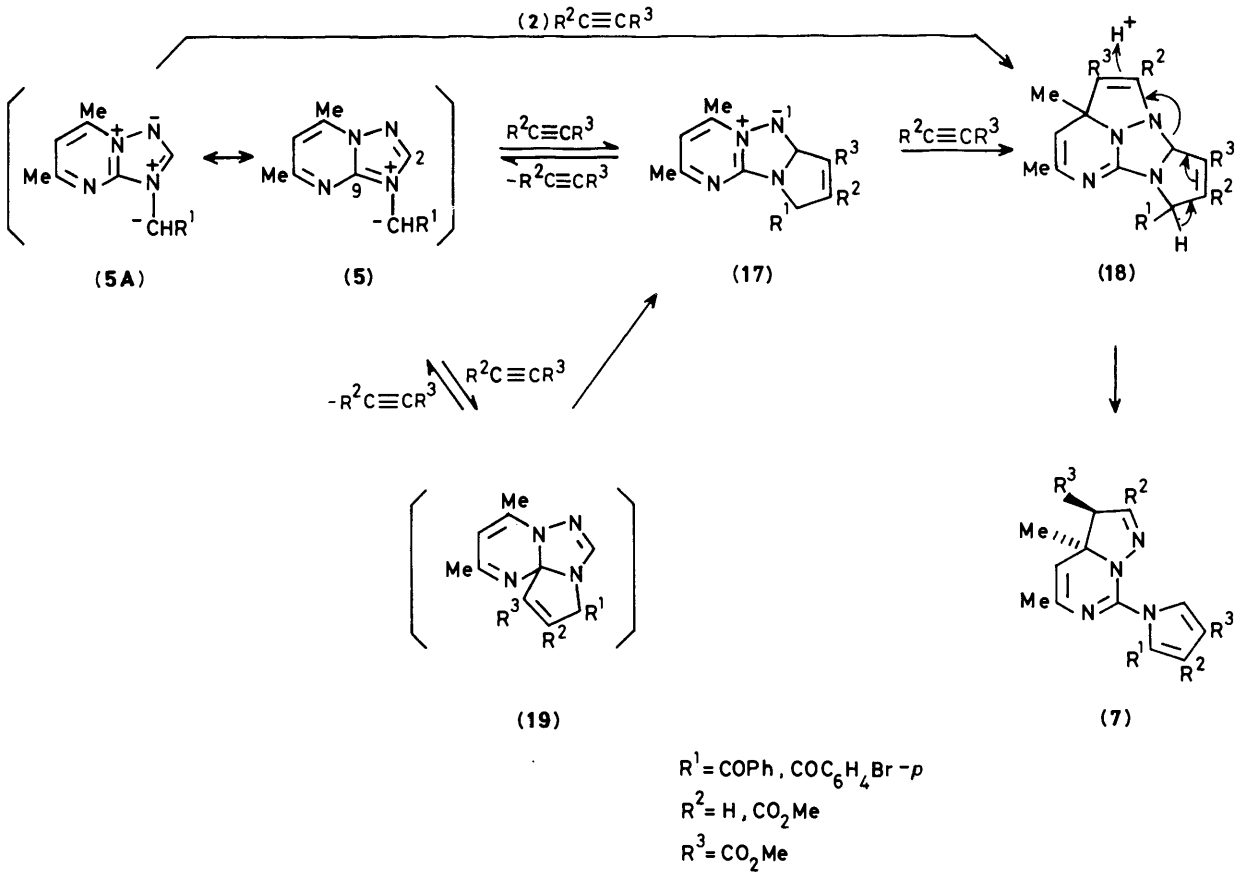
Possible mechanisms for the formation of compounds (**7**) are shown in Scheme 5. The shortest pathway consists of the double 1,3-dipolar cycloaddition of a diylide (**5A**), one of the resonance structures of the ylide (**5**). The diylide (**5A**) reacts with two molecules of the acetylene at two different sites to form a tetracyclic adduct (**18**) followed by ring-opening under basic conditions to give (**7**). The second pathway has many stages and consists of cycloaddition between the ylide carbanion of (**5**) and the bridged carbon (C–9) to form a 1:1 adduct (**19**), which isomerises to the more stable compound (**17**). The second cycloaddition affords the 1:2 adduct (**18**). The first cycloaddition may occur at the ylide carbanion and C(2) to form the 1:1 adduct (**17**).

In order to differentiate between the reaction mechanism described above, we performed *ab initio* molecular orbital calculation with the STO-3G basis set. [1,2,4]Triazolo[1,5-*a*]pyrimidinio-3-methylide (**20**) and formylmethylide (**21**) and triazolinopyrimidinium ylide (**22**) were selected as models for compounds (**5**) and (**17**) to simplify the calculation. The geometries were optimised under constraint to C_s symmetry (planar structure). The frontier molecular orbital (HOMO, LUMO) energies and coefficients of the ylides (**20**)—(**22**) are depicted in Figure 2.

Generally the ylides are electron-rich species possessing high-lying HOMO and LUMO, and react readily with electron-



Scheme 4.



Scheme 5.

deficient alkenes or acetylenes. All the reactions of ylides with electron-deficient dipolarophiles are controlled by the HOMO of the ylide.[5] The ylides (**5**) did not react with electron-rich acetylenes such as phenylacetylene. The HOMO energy (−0.164 320 2 a.u.) of the ylide (**22**) is lower than that of the starting ylide (**21**) (−0.127 835 4 a.u.). According to the frontier orbital theory, this result suggested that the first cycloaddition to form the 1:1 adduct (**17**) is faster than the second one to form the 1:2 adduct (**18**). Very recently Sun reported the double cycloaddition of 3-phenylsydnone with *N*-phenylmaleimide.[6]

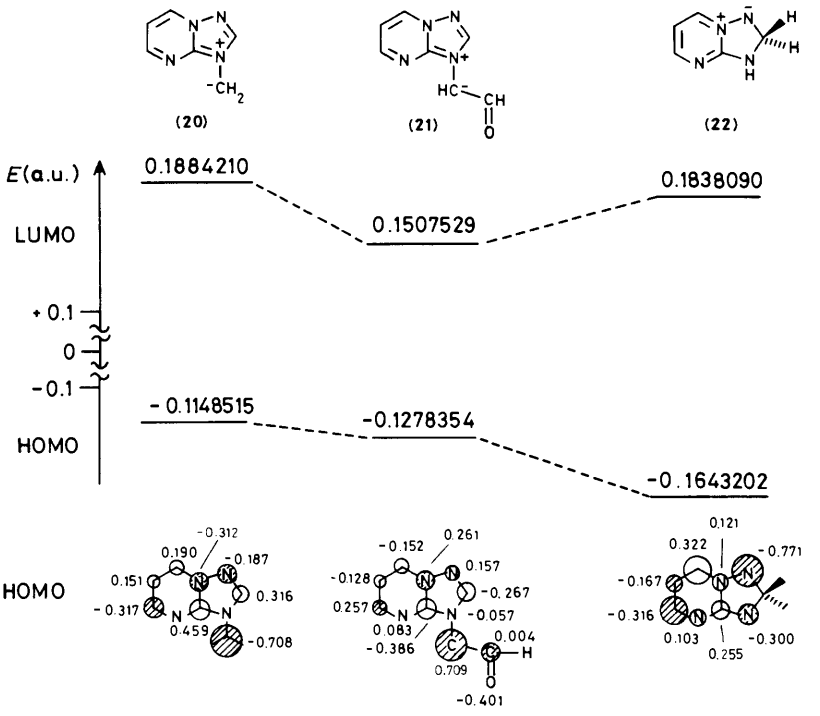
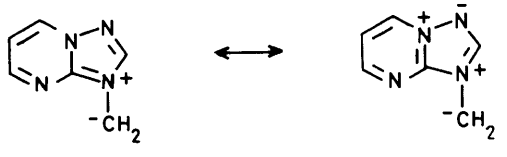


Figure 2. The frontier orbital energies and their coefficients for ylides calculated by the *ab initio* (STO-3G) method

The 1:2 adduct of sydnone:maleimide was produced even by use of a large excess of the sydnone. The reaction mechanism was explained by the assumption that the second cycloaddition is extremely fast. The HOMO energies of the starting ylide and the 1:1 adduct suggested that Sun's explanation was not applicable to the present reaction. If the second cycloaddition is slower than the first, as suggested from the calculations, the newly formed ylide (**17**) or its degradation products should be isolable. However, despite many attempts, they were not isolated. We explain the formation mechanism of the 1:2 adduct in terms of the equilibrium between the 1:1 adduct (**17**) and the starting materials, (**5**) and the acetylenic dipolarophile. Retro-1,3-dipolar cycloadditions are known in the adducts of azomethine ylides.[7]

The site-selectivity of the double cycloaddition is discussed below. On the basis of the HOMO coefficients of the ylide (**21**), the acetylene should react with ylide (**5**) at the ylide carbanion and C(9) to form (**19**). However, since C(9) binds to three nitrogen atoms in compound (**19**), the newly formed C–C bond would be thermodynamically unstable and would undergo breakage followed by recombination with C(2) to form (**17**), or alternatively the C–C bond between C(9) and the acetylene would not be formed but the C(2)-acetylene bond would be primarily formed. The calculated result for (**22**) shows that the intermediate ylide (**17**) reacts with the acetylene at N(1) and C(7), and agrees with the experimental selectivity. The mechanism in which the ylide (**5**) reacts simultaneously with two molecules of the acetylene in the diylide form (**5A**) would not occur because of the low contribution of the resonance structure (**19A**) [(**19A**):(**19**) = 1:4.2][8] and disadvantages associated with entropy.



(**19**) (**19A**)

The observed regioselectivity of the reaction agrees with the calculated results.

Experimental

M.p.s were determined on a Yanagimoto micro melting point apparatus and are uncorrected. I.r. spectra were recorded on a JASCO A-1 i.r. spectrophotometer. ^{1}H N.m.r. spectra were obtained on Hitachi R-20B (60 MHz), Bruker WH-400 (400 MHz), JEOL FX-100 (100 MHz) or JEOL FX-270 (270 MHz) spectrometers with tetramethylsilane as an internal standard. ^{13}C N.m.r. spectra were obtained using a JEOL FX-100 spectrometer. Mass spectra were obtained using a JEOL-D 300 spectrometer with a direct insertion probe, at 70ev. All exact mass determinations were obtained on the JMA 2000 online system. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University.

Reaction of 5,7-*Dimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinio*-3-*phenacylide* (**5a**) *with Methyl Propiolate* (*MP*).—Triethylamine (111 mg, 1.1 mmol) was added in portions to a solution of 5,7-dimethyl-3-phenacyl[1,2,4]triazolo[1,5-*a*]pyrimidinium bromide (**4a**) (347 mg, 1 mmol) and MP (126 mg, 1.5 mmol) in dry acetonitrile (10 ml) at ice-bath cooling temperature. The mixture was stirred at 0 °C for 1.5 h. The solvent was evaporated off under reduced pressure, and the residue was extracted several times with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The residual solid was purified by column chromatography on silica-gel (hexane–$CHCl_3$ 2:1) to give the pyrimidine (**6a**) (147 mg, 18.5%) and the pyrazolopyrimidine (**7a**) (115 mg, 26.5%). Fractional recrystallisation of (**7a**) gave the major diastereoisomer (**7a**$_1$) as colourless needles, m.p. 150—152 °C; *m/z* 434 (M^+), $\nu_{max.}$(KBr) 1 720 and 1 750 cm^{-1}; δ_C($CDCl_3$) 184.4s, 166.9s, 163.6s, 142.5s, 141.5d, 141.3s, 137.4s, 133.2s, 132.6d, 132.4d, 129.5d, 128.3d, 121.6d, 116.6s, 105.7d, 63.9d, 63.8s, 52.4q, 51.4q, 28.1q, and 22.2q p.p.m. (Found: C, 63.35; H, 5.1; N, 12.7. $C_{23}H_{22}N_4O_5$ requires C, 63.6; H, 5.1; N, 12.9%).

Reaction of 5,7-*Dimethyl*-[1,2,4]*triazolo*[1,5-a]*pyrimidinio*-3-*phenacylide* (**5a**) *with Dimethyl Acetylenedicarboxylate* (*DMAD*).—Triazolopyrimidinium bromide (**4a**) (347 mg, 1 mmol) was treated with triethylamine (111 mg, 1.1 mmol) and then with DMAD (213 mg, 1.5 mmol) in a way similar to that described above to give (**6a**) (trace) and (**7c**) (39%). Fractional recrystallisation of (**7c**) from diethyl ether gave the major diastereoisomer (**7c**$_1$) as colourless needles, m.p. 132—133 °C; *m/z* 550 (M^+); $\nu_{max.}$(KBr) 1 730 and 1 755 cm^{-1}; δ_C($CDCl_3$) 185.7s, 166.2s, 163.7s, 162.4s, 161.1s, 142.5s, 142.4s, 139.8s, 137.3s, 132.8d, 132.3s, 130.6d, 129.5d, 128.0d, 124.1s, 115.3s, 107.5d, 67.3s, 62.2d, 52.7q, 52.5q, 51.9q, 51.8q, 27.3q, and 22.1q p.p.m. (Found: C, 59.0; H, 4.8; N, 10.3. $C_{27}H_{26}N_4O_9$ requires C, 58.9; H, 4.8; N, 10.2%).

Reaction of 5,7-*Dimethyl*-[1,2,4]*triazolo*[1,5-a]*pyrimidinio*-3-p-*bromophenacylide* (**5b**) *with MP*.—The triazolopyrimidinium salt (**4b**) (426 mg, 1 mmol) was treated with triethylamine and MP in a way similar to that described above to give compounds (**6b**)[1] (6%) and (**7b**) (21.5%). Fractional recrystallisation of compounds (**7b**) from diethyl ether gave a major diastereoisomer (**7b**$_1$) as colourless needles, m.p. 172—174 °C; *m/z* 512 (M^+), 514 ($M^+ + 2$); $\nu_{max.}$(KBr) 1 724 and 1 750 cm^{-1}; (Found: C, 54.0; H, 4.3; N, 10.7. $C_{23}H_{21}BrN_4O_5$ requires C, 53.8; H, 4.1; N, 10.9%).

Preparation of 3-*Phenacyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium Bromide*.—A solution of [1,2,4]triazolo[1,5-*a*]pyrimidine[9] (1.2 g, 10 mmol) and phenacyl bromide (10 g, 50 mmol) in dry acetone (30 ml) was refluxed for 3 h. The precipitated solid was collected, dried, and recrystallised from ethanol–diethyl ether to give the product (**9**) (1.9 g, 60%) as colourless prisms, m.p. 264—265 °C; *m/z* 239 (M^+ − HBr); $\nu_{max.}$(KBr) 1 706 cm^{-1}; δ_H ([$^2H_6$]DMSO, 60 MHz) 10.00 (dd, 1 H, $J_{5,6}$ 6.8 Hz, $J_{5,7}$ 2.1 Hz), 9.81 (s, 1 H), 9.43 (dd, 1 H, $J_{7,6}$ 4.7 Hz, $J_{7,5}$ 2.1 Hz), 8.28—7.58 (m, 6 H), and 6.35 (s, 2 H) (Found: C, 48.95; H, 3.45; N, 17.6. $C_{13}H_{11}BrN_4O$ requires C, 48.9; H, 3.5; N, 17.55%).

Reaction of [1,2,4]*Triazolo*[1,5-a]*pyridinio*-3-*phenacylide*.—A procedure similar to that used for the 5,7-dimethyl-[1,2,4]triazolo[1,5-*a*]pyrimidinio-3-phenacylide with DMAD gave the pyrazolopyrimidine (**12**) (28%); m.p. 153—155 °C (ethyl acetate–hexane), *m/z* 520 (M^+); $\nu_{max.}$(KBr) 1 725 and 1 750 cm^{-1}; δ_H($CDCl_3$, 270 MHz) 8.13 (d, 1 H, *J* 5.9 Hz), 8.08 (s, 1 H), 8.04 (d, 1 H, *J* 5.9 Hz), 7.42—7.86 (m, 5 H), 3.89 (s, 3 H), 3.86 (s, 3 H), 3.73 (s, 3 H), and 3.30 (s, 3 H) (Found: C, 57.4; H, 3.9; N, 10.5. $C_{25}H_{20}N_4O_9$ requires C, 57.7; H, 3.9; N, 10.8%).

Hydrolysis of 3,3*a*-*Dihydro*-7-*pyrrol*-1-*ylpyrazolo*[1,5-c]*pyrimidine Derivatives* (**7a**) *and* (**7c**).—0.1M Hydrochloric acid (2 ml) was added to a solution of compound (**7a**) [or (**7c**)] (0.2 mol) in methanol (2 ml). The mixture was refluxed for 1 h, cooled to room temperature, evaporated under reduced pressure, and the residue extracted several times with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to afford the product which was purified by preparative t.l.c. (hexane–ethyl acetate 1:1) to give compound (**8a**) [or (**8c**)].

Compound (**8a**) (64.4%), m.p. 149—151 °C (from hexane–ethyl acetate), *m/z* 229 (M^+); $\nu_{max.}$(KBr) 3 256 and 1 714 cm^{-1}; δ_H ([$^2H_6$]acetone, 400 MHz) 11.6 (br s, 1 H), 7.93—7.56 (m, 5 H), 7.79 (d, 1 H, *J* 1.4 Hz), 7.18 (d, 1 H, *J* 1.4 Hz), and 3.79 (s, 3 H); δ_C($CDCl_3$) 185.4s, 164.4s, 137.4s, 132.5d, 131.4s, 129.4d, 129.0d, 128.5d, 119.9d, 118.2s, and 51.4q p.p.m. (Found: C, 68.1; H, 4.8; N, 6.1. $C_{13}H_{11}NO_3$ requires C, 68.0; H, 4.8; N, 6.1%).

Compound (**8c**) (61%), m.p. 110—113 °C (from hexane–ethyl acetate), *m/z* 287 (M^+); $\nu_{max.}$(KBr) 3 248, 1 748, and 1 724 cm^{-1}; δ_H($CDCl_3$, 60 MHz) 10.17 (br s, 1 H), 7.80—7.33 (m, 6 H), 3.78 (s, 3 H), and 3.33 (s, 3 H) (Found: C, 62.45; H, 4.6; N, 4.9. $C_{15}H_{13}NO_5$ requires C, 62.7; H, 4.6; N, 4.9%).

Table 2. Atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Br	4 433(1)	3 580(0.7)	10 865(0.7)
O(1)	8 386(7)	−3 463(4)	7 684(4)
O(2)	7 531(7)	−2 043(4)	6 461(4)
O(3)	7 144(6)	4 933(4)	4 303(4)
O(4)	8 213(8)	3 836(5)	3 383(4)
O(5)	10 985(6)	2 388(4)	8 793(4)
N(1)	11 878(7)	998(4)	6 464(4)
N(2)	9 808(7)	347(4)	7 492(4)
N(3)	8 144(7)	312(5)	7 642(5)
N(4)	9 810(7)	2 142(4)	6 482(4)
C(1)	11 645(9)	−949(6)	7 288(5)
C(2)	12 292(9)	−129(6)	6 615(5)
C(3)	10 580(9)	1 135(5)	6 838(5)
C(4)	7 717(9)	−689(6)	8 080(6)
C(5)	9 011(9)	−1 506(6)	8 231(5)
C(6)	10 651(9)	−665(5)	8 035(5)
C(7)	9 444(9)	2 531(6)	5 399(5)
C(8)	8 564(8)	3 449(5)	5 290(5)
C(9)	8 345(9)	3 633(6)	6 343(6)
C(10)	9 113(9)	2 801(6)	7 059(5)
C(11)	13 488(10)	−301(7)	5 939(7)
C(12)	11 879(10)	−324(6)	9 141(6)
C(13)	8 281(9)	−2 464(6)	7 448(6)
C(14)	6 741(12)	−2 893(7)	5 659(7)
C(15)	7 938(9)	4 075(6)	4 230(6)
C(16)	6 453(11)	5 579(6)	3 282(6)
C(17)	9 531(9)	2 717(6)	8 269(5)
C(18)	8 275(8)	3 020(5)	8 818(5)
C(19)	8 907(9)	3 535(6)	9 817(6)
C(20)	7 774(9)	3 708(6)	10 420(5)
C(21)	5 993(9)	3 363(6)	10 022(6)
C(22)	5 331(9)	2 849(6)	9 042(6)
C(23)	6 453(9)	2 692(6)	8 433(5)

Reaction of Compound (**5b**) *with Diphenylcyclopropenone*.—Triethylamine (77.8 mg, 0.77 mmol) was added in portions to a solution of 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinio-3-*p*-bromophenacylide (**5b**) (300 mg, 0.7 mmol) and diphenylcyclopropenone (159 mg, 0.77 mmol) in dry acetonitrile (10 ml) at ice-bath temperature. The mixture was stirred at 0 °C for 2 h and then at room temperature for 5 h. The solvent was evaporated under reduced pressure and the residue was extracted several times with chloroform. The extracts were washed with water dried ($MgSO_4$), and evaporated under reduced pressure to afford the products which were purified by preparative t.l.c. (hexane–ethyl acetate 1:1) to give (**16**) (211 mg, 74.5%) and (**15**) (65 mg, 62.5%). Compounds (**15**) and (**16**) were identical with authentic samples by i.r., ^1H n.m.r., and mixed m.p.

Reaction of compound (**5b**) *with Dimethyl Fumarate* (*or Dimethyl Maleate*).—Triethylamine (77.8 mg, 0.77 mmol) was added in portions to a solution of 5,7-dimethyl-[1,2,4]triazolo[1,5-*a*]pyrimidinio-3-*p*-bromophenacylide (**5b**) (300 mg, 0.7 mmol) and dimethyl maleate (112 mg, 0.77 mmol) in dry acetonitrile (10 ml) at ice-bath temperature. The mixture was stirred at 0 °C for 1.5 h and then at room temperature for 18 h. It was then evaporated under reduced pressure and the residue extracted several times with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to afford the products which were purified by preparative t.l.c. (hexane–ethyl acetate 1:1) to give (**14**) (62 mg, 17.5%) as a mixture of diastereoisomers (7:3 ratio). The

reaction using dimethyl maleate gave the similar result (yield 28%, same diastereoisomer ratio). The product (**14**) was recrystallised from hexane–ethyl acetate to give colourless needles (as a mixture of diastereoisomers), m.p. 90—91 °C, *m/z* 490(M^+); $\nu_{max.}$(KBr) 2 240, 1 740, and 1 720 cm^{-1}; δ_H($CDCl_3$, 100 MHz) 7.96—7.53 (m, 4 H), 6.75 (s, 1 H), 6.50 (0.7 H, *J* 6.6 Hz), 6.4 (d, 0.3 H, *J* 6.6 Hz), 3.97 (dd, 1 H, *J* 6.6, 7 Hz), 3.66 (s, 2.1 H), 3.65 (s, 2.1 H), 3.63 (s, 0.9 H), 3.62 (s, 0.9 H), 3.04 (dd, 1 H, *J* 17, 7 Hz), 2.72 (dd, 1 H, *J* 17, 7 Hz), and 2.40 (s, 6 H) (Found: C, 51.3; H. 4.4; N, 11.2. $C_{21}H_{21}BrN_4O_5$ requires C, 51.55; H, 4.3; N, 11.45%).

Crystal Data for Compound (**7b$_1$**).—$C_{23}H_{21}BrN_4O_5$, M = 513, triclinic, space group $P\bar{1}$; a = 8.021(5), b = 11.825(5), c = 12.657(5) Å, α = 83.50(3), β = 104.61(4), γ = 100.89(4)°, D_x = 1.50 g cm^{-3}, Z = 2 and μ(Mo-K_α) = 19.6 cm^{-1}. The cell dimension and intensities were measured on a Syntex R3 four-circle diffractometer with graphite-monochromated Mo-K_α radiation with ω-scan mode within 2θ less than 45°. A total of 2 980 independent reflections were collected, among which 2 641 reflections [$I \geqq 1.96\sigma(I)$] were stored as observed. The structure was solved by the heavy-atom method. The hydrogen atoms were found on a different Fourier map. A block-diagonal least-squares method was applied to the refinement with anisotropic temperature factors for the non-hydrogen atoms and isotropically for the hydrogen atoms. The final R-value was 0.066. Atomic co-ordinates are given in Table 2. Tables of bond lengths, bond angles, and thermal parameters are available on request from the Cambridge Crystallographic Data Centre.*

* See Instructions for Authors (1987), para. 5.6.3., *J. Chem. Soc., Perkin Trans. 1*, 1987, Issue 1.

Acknowledgements

The *ab initio* molecular orbital calculations were carried out on a HITAC-M200H computer, at the Institute for Molecular Science, with a GAUSSIAN 70 Program.

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Received 30*th September* 1986; *Paper* 6/1932