Synthesis and Selective Reactions of v-Triazolo-[1,5-*b*]pyridazinium Salts with Nucleophiles. A Facile Access to Functionalized Ethenyl-1,2,3-triazoles [1]

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v-Triazolo[1,5-*b*]pyridazinium salts **5a-c** synthesized from α-pyridazinyl ketone arylhydrazones and 2,4,4,6-tetrabromocyclohexa-2,5-dien-1-one (TBB) reacted selectively with nucleophiles to yield - besides substituted derivatives **6** - ring-opened cyano compound **9** and/or v-triazoles containing olefinic side chain **10-12**. Mechanistic considerations reveal that cation **5** reacts with nucleophiles predominantly at C-7 unless other positions are especially activated. This selectivity proved to be in good agreement with results of semiempirical quantum chemical calculations.

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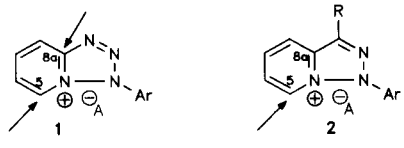
In the course of our earlier work on fused azolium salts [1,2,3,4] we found that tetrazolopyridinium salts **1** synthesized from α-pyridyltriazines with 2,4,4,6-tetrabromocyclohexa-2,5-dien-1-one (tribromophenol bromine; "TBB") easily react with nucleophiles at the carbon atoms adjacent to the positive bridgehead nitrogen atom to give two types of products in most cases: reaction at C-5 results in tetrazolyldiene derivatives whereas the attack at C-8a leads to nitrogen elimination. One of our earlier studies [4], however, revealed that the deaza analogues of **1**: v-triazolopyridinium salts (**2**) obtained from α-pyridyl ketone hydrazones by *N*-bromosuccinimide as described by Kuhn [5] react with nucleophiles specifically at C-5 to give triazolyldienes only.

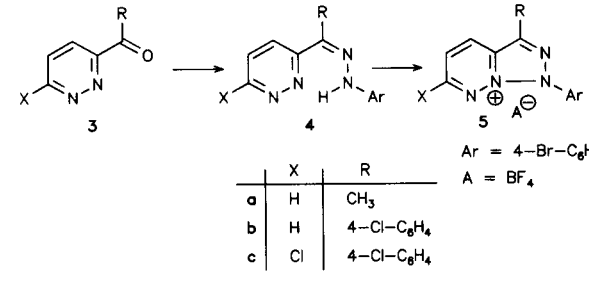
Scheme I



As a continuation of these studies we decided to extend the above ring closure reaction (called "cyclodehydrogenation") to the synthesis of v-triazolo[1,5-*b*]pyridazinium salts **5**. This fused heteroaromatic ring system has the structural peculiarity that position 5 which proved to be the most reactive site in the related azolium salts **1** and **2** is now blocked by the presence of the nitrogen atom of the pyridazine moiety. Thus, we expected that the relatively activated position 7 (*in para* compared to the positive nitrogen atom) can also take part in these conversions.

The v-triazolo[1,5-*b*]pyridazine ring system as a neutral compound has already been described [6] whereas the related positively charged *N*-aryl derivatives has not yet been reported. For its synthesis, we applied our earlier elaborated procedure starting from the appropriate ketone **3** which was first converted to its arylhydrazone **4** and this compound was then treated with TBB to yield the ring closed product **5**.

Scheme II



	X	R
a	H	CH_3
b	H	4-Cl-C_6H_4
c	Cl	4-Cl-C_6H_4

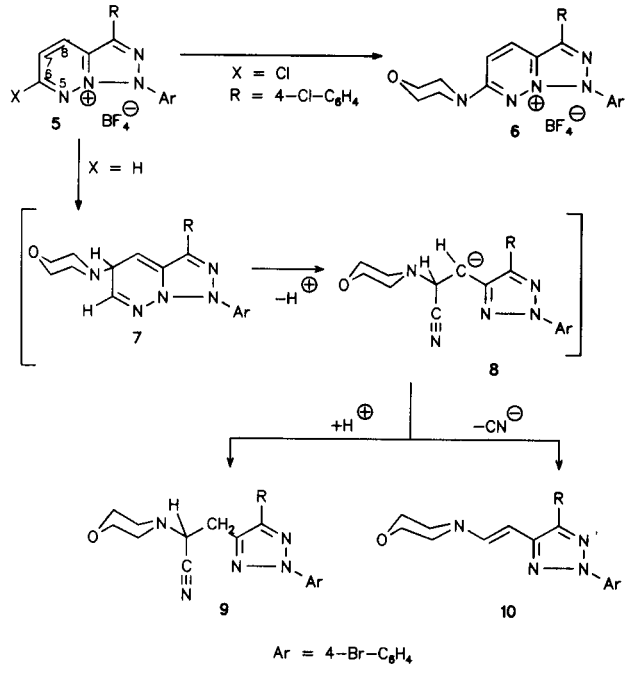
Ar = 4-Br-C_6H_4
A = BF_4

Ketone **3a** was already known from the literature [7] whereas ketones **3b,c** have now been prepared from 3-cyanopyridazine using the corresponding Grignard reagent. Reaction with *p*-bromophenylhydrazine with ketone **3a-c** following the procedure described for the analogous pyridine compounds [8] afforded hydrazones **4a-c** as yellow crystals in good yields.

Hydrazones **4a-c** readily reacted with TBB or NBS at 40° and resulted in the desired v-triazolopyridazinium salts as colorless crystals. The ring closure itself was convincingly revealed - besides the routine infrared data -by significant downfield shifts of the pyridazine protons in ^1H nmr in accordance with the extension of the heteroaromatic ring current (see Experimental).

While v-triazolopyridazinium salt **5c** containing a chlorine substituent in position 6 reacted with morpholine by a simple nucleophilic displacement and yielded 1-(4-chlorophenyl)-3-(4-bromophenyl)-6-morpholino-v-triazolopyridazinium salt **6** in good yield, the derivatives unsubstituted in the pyridazine moiety, **5a,b**, underwent ring opening of

Scheme III

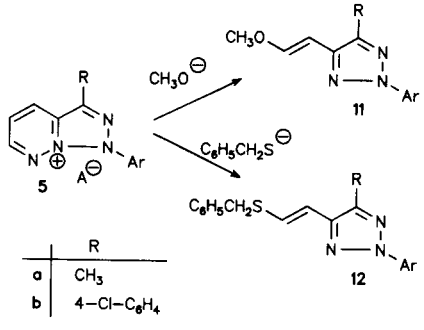


the pyridazine ring [9] and resulted in mixtures containing two products; the 5-*R* substituted 4-(β-cyano-β-morpholinoethyl)-2-*p*-bromophenyl-v-triazole **9** containing the cyano group and the v-triazolylenamine derivative **10**. The ratio of these products was significantly different in the two cases; methyl compound **5a** gave predominantly **9a** whereas the aryl derivative **5b** yielded triazolyl enamine **10b** as the major product and **9a** was found only in traces.

The simultaneous formation of **9** and **10** may be interpreted so that the nucleophile attacks the bicyclic heteroaromatic cation at position 7 to yield first pseudo base **7**. This intermediate can loose a proton under the basic conditions and the resulting anion easily undergoes ring opening to afford the open-chain species **8** containing the cyano group which either can take up a proton to yield **9** or can eliminate cyanide anion and lead to enamine **10**.

The different reactivities of the alkyl and aryl substituted triazolium salts, **5a** and **5b** respectively, may well be due to the different basicity of the carbanion caused by the different electron demands of these two substituents. In order to verify this mechanistic hypothesis we tried to react **5a** with morpholide anion generated by sodium hydride in tetrahydrofurane in order to minimize the presence of protons; this condition should suppress formation of **9** according to the above mechanistic picture. We found that, as expected, exclusively olefin **10a** was formed in good yield. Similarly, reaction of **5a** and **5b** with alcoholates or thiolates afforded olefines **11a,b** and **12a,b** respectively, as the only products.

Scheme IV



This finding indicates that the attack of the nucleophile which was found with the examples studied earlier (*e.g.* with the tetrazolo pyridinium cation [4]) to take place at positions 5 and 8a is reoriented - as expected - selectively to position 7 (or to position 6 in a special case).

Table I

Structures and Heats of Formation of the Possible Pseudo Bases Formed from v-Triazolo[1,5-*b*]pyridazinium Cation with Nucleophiles (Nu) [a]

a	b	c	d
96.15 kcal/mol	110.28 kcal/mol	92.04 kcal/mol	114.70 kcal/mol

[a] The calculations were carried out by using the MNDO method [10,11]. Geometries were fully optimized in each case. For simplicity, the group introduced by the nucleophile (Nu) as well as the R substituents were replaced by hydrogen atoms.

For interpretation of this selectivity, consideration of the stabilities of the possible pseudo bases (whilch are supposed to be formed from **5** under thermodynamic control) seemed of special interest. These structures and the calculated heats of formation are summarized in Table I. This table shows that the zwitterionic pseudo bases **b** and **d** are obviously less stable alternatives and between the more stable **a** and **c** there is still a certain difference in favor to the latter. Thus, upon these data, formation of pseudo base **c** - *i.e.* intermediate **7** formed by the attack of the nucleophile at C-7 - seems the most probable which is in fact in agreement with the experimental findings.

The above results, besides their contribution to ring openings of fused azolium salts, provide a fairly simple route to the differently functionalized ethenyl-1,2,3-triazoles, a hitherto unexplored group of compounds.

EXPERIMENTAL

Melting points were determined on a Büchi apparatus and are uncorrected. The ir spectra were recorded on Specord IR-75 equipment. The ^{1}H nmr spectra were recorded on Varian XL-100

instrument at ambient temperature.

3-*p*-Chlorobenzoylpyridazine (**3b**).

To a mixture of 3-cyanopyridazine [12] (1.05 g, 10 mmoles) and ether (5 ml), an etheral solution of *p*-chlorophenylmagnesium bromide (prepared from 0.29 g of magnesium, 2.3 g of *p*-chlorobromobenzene and 30 ml of ether) was added and the mixture was allowed to stand at 0° overnight. The reaction mixture was first poured onto 10% ammonium chloride solution (10 ml) and was then acidified with 20% sulphuric acid to *p*H 1. The mixture was shaken for 2 hours and was finally neutralized with 20% sodium hydroxide to *p*H 8. Separation of the organic layer, extraction of the aqueous layer with two portions of ether (2 x 50 ml), evaporation of the solvent and recrystallization of the residue from 96% ethanol afforded colorless prisms, 1.7 g (78%), mp 112-114°; ir (potassium bromide): 3080, 3050, 1660, 1580, 1480, 1400, 1375, 1300, 1200, 1090, 1000, 850, 820, 750, 780 cm^{-1}; ^1H nmr (60 MHz, DMSO-d_6): δ 9.55 (1H, d, 4-H), 8.4-7.6 (6H, m, 5,6-H, and Ar).

Anal. Calcd. for $C_{11}H_7ClN_2O$: C, 60.43; H, 3.23; N, 12.81; Cl, 16.22. Found: C, 60.48; H, 3.59; N, 12.61; Cl, 15.70.

3-*p*-Chlorobenzoyl-6-chloropyridazine (**3c**).

This compound was prepared from a mixture of 3-cyano-6-chloropyridazine [13] (2.8 g, 20 mmoles) and ether (10 ml) by addition of the Grignard reagent prepared from 0.58 g of magnesium, 4.6 g of *p*-chlorobromobenzene in 60 ml of ether according to the previous procedure. The crude product was recrystallized from 96% ethanol to give 3.8 g (75%) of product, mp 109-112°; ir (potassium bromide): 3070, 3040, 1660, 1580, 1550, 1380, 1330, 1270, 1150, 1080, 1050, 920, 860, 770 cm^{-1}.

Anal. Calcd. for $C_{11}H_6Cl_2N_2O$: C, 52.20; H, 2.39; N, 11.07; Cl, 28.02. Found: C, 52.49; H, 2.65; N, 11.09; Cl, 27.96.

3-Acetylpyridazine *p*-Bromophenylhydrazone (**4a**).

A mixture of 3-acetylpyridazine (1.22 g, 10 mmoles) *p*-bromophenylhydrazine hydrochloride (2.26 g, 12 mmoles) and ethanol (15 ml) was heated under reflux for 3 hours. A crystalline mass was formed which was filtered off and added to a sodium hydroxide (5%) solution. Extraction with chloroform and recrystallization of the residue of the organic layer ethanol gave 2.05 g (70%) of product, mp 222-224°; ir (potassium bromide): 3250, 3090, 1590, 1480, 1430, 1400, 1380, 1280, 1250, 1160, 1150, 1130, 1060, 990, 960, 820, 810, 740 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.75 (1H, s, NH), 9.1 (1H, d, 6-H), 8.35 (1H, d, 4-H), 7.5 (1H, d, 5-H), 7.3 (4H, m, Ar), 2.55 (3H, s, CH_3).

Anal. Calcd. for $C_{12}H_{11}BrN_4$: C, 49.50; H, 3.81; N, 19.24; Br, 27.44. Found: C, 49.50; H, 3.85; N, 19.28; Br, 27.68.

3-*p*-Chlorobenzoylpyridazine *p*-Bromophenylhydrazone (**4b**).

To a solution of 3-*p*-chlorobenzoylpyridazine **3b** (2.18 g, 10 mmoles) was added a solution of *p*-bromophenylhydrazine hydrochloride (2.6 g) and sodium acetate (1.0 g) in ethanol (20 ml), and the reaction mixture was stirred for 2 hours. Water (10 ml) was then added and the mixture was extracted with chloroform. The residue obtained from the organic layer was recrystallized from acetic acid to give 2.6 g (66%) of product, mp 206-211°; ir (potassium bromide): 3270, 3080, 1580, 1550, 1500, 1480, 1430, 1280, 1250, 1130, 1080, 1010, 821 cm^{-1}.

Anal. Calcd. for $C_{17}H_{12}BrClN_4$: C, 52.67; H, 3.12; N, 14.45. Found: C, 52.39; H, 3.01; N, 14.25.

6-Chloro-3-*p*-chlorobenzoylpyridazine *p*-Bromophenylhydrazone (**4c**).

This compound was prepared from a solution of 6-chlorobenzoylpyridazine **3c** (2.53 g, 10 mmoles) and a solution of *p*-bromophenylhydrazine hydrochloride (2.6 g) and sodium acetate (1.0 g) in absolute ethanol (30 ml) according to the above procedure. Recrystallization from a mixture of chloroform and ethanol afforded 3.2 g of product (76%), mp 195-198°; ir (potassium bromide): 3200, 3070, 1590, 1580, 1550, 1520, 1500, 1480, 1400, 1390, 1340, 1240, 1130, 1080, 1060, 1010, 820 cm^{-1}; ^1H nmr (DMSO-d_6): δ 8.85 (1H, s, NH), 8.32 (1H, d, 5-H), 7.55 (1H, d, 4-H), 7.53 and 7.13 (4H, AA'BB', 4-chlorophenyl), 7.35 (4H, m, 4-bromophenyl).

Anal. Calcd. for $C_{17}H_{11}BrCl_2N_4$: C, 48.37; H, 2.63; N, 13.27; Cl, 16.79; Br, 18.93. Found: C, 48.40; H, 2.64; N, 13.29; Cl, 16.51; Br, 18.99.

1-Methyl-3-*p*-bromophenyl-v-triazolo[1,5-*b*]pyridazinium Fluoborate (**5a**).

To a solution of 3-acetylpyridazine *p*-bromophenylhydrazone **4a** (1.5 g, 5 mmoles) in dichloroethane (120 ml) was added tribromophenol bromine (6.15 g, 15 mmoles) in portions at 0° with stirring. A red solution was formed temporarily and, in 10 minutes approximately, a precipitate commenced. The stirring was continued at room temperature for an additional 30 minutes. Ether (50 ml) was then added and the precipitate was filtered off. The orange crystals (primarily formed perbromide salt) were suspended in nitromethane (5 ml), cyclohexene (0.55 ml) was added to this suspension, and it was stirred at room temperature for 30 minutes. Ether (5 ml) was added again and the colourless precipitate was filtered off to give 1.25 g (67%) of the bromide salt. This bromide salt was converted to the fluoborate derivative as follows: to a suspension of bromide salt (1.2 g) in acetonitrile (30 ml) 40% fluoboric acid (1 ml) was added whereupon a clear solution was formed from which the fluoborate was precipitated by addition of ether. Filtration and recrystallization from acetonitrile-ether gave 1.1 g of product, mp 232-235°; ir (potassium bromide): 3090, 3040, 3000, 2940, 1630, 1610, 1570, 1550, 1480, 1410, 1380, 1350, 1280, 1270, 1080, 820 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.5 (2H, d, 6,8-H), 8.3 (1H, dd, 7-H), 8.1 (4H, m, 4-bromophenyl), 2.9 (3H, s, CH_3).

Anal. Calcd. for $C_{12}H_{10}BrN_4BF_4$: C, 38.23; H, 2.67; N, 14.86; Br, 21.20. Found: C, 38.33; H, 2.75; N, 14.76; Br, 21.11.

1-*p*-Chlorophenyl-3-*p*-bromophenyl-v-triazolo[1,5-*b*]pyridazinium Fluoborate (**5b**).

This compound was prepared according to the above procedure starting from the appropriate hydrazone **4b** (3.87 g; 10 mmoles) and tribromophenol bromide (12.3 g). The resulting bromide salt (2.7 g, 57%) was converted to the fluoborate salt as above to give 2.04 g (43%) of product, mp 246-252°; ir (potassium bromide): 3090, 3040, 1600, 1540, 1480, 1420, 1270, 1070, 1010, 990, 950, 830 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.53 (1H, d, J = 9.1 Hz), 9.43 (1H, d, 8-H), 8.32 (dd, 1H, H-7), 8.20 and 7.33 (4H, AA'BB', 4-chlorophenyl), 8.0 (4H, m, 4-bromophenyl).

Anal. Calcd. for $C_{17}H_{11}ClBrN_4BF_4$ (473.50): C, 43.12; H, 2.34; N, 11.83; Br, 16.88; Cl, 7.49. Found: C, 43.30; H, 2.66; N, 11.47; Br, 16.76; Cl, 7.36.

1-*p*-Chlorophenyl-3-*p*-bromophenyl-6-chloro-v-triazolo[1,5-*b*]pyridazinium Fluoborate (**5c**).

A mixture of 3-*p*-chlorobenzoyl-6-chloropyridazine *p*-bromophenylhydrazone **4c** (2.1 g, 5 mmoles), *N*-bromosuccinimide (2.7 g) and dichloromethane (60 ml) was stirred at room temperature for 3 hours. Ethyl acetate (20 ml) was added and the resulting orange perbromide salt was filtered off. Treatment with cyclohexene as above gave bromide salt (1.5 g, 60%) which was converted to the fluoborate derivative according to the analogous cases of **5a,b**. Recrystallization from acetonitrile-ether afforded 1.30 g (51%) of product, mp 271-275°; ^{1}H nmr (deuterioacetonitrile): δ 9.05 (1H, d, J = 9.50 Hz, 7-H), 8.18 (1H, d, 8-H), 8.05 and 7.72 (4H, AA'BB', 4-chlorophenyl), 7.97 (4H, m, 4-bromophenyl); ir (potassium bromide): 3090, 1600, 1530, 1480, 1410, 1310, 1290, 1250, 1180, 1170, 1150, 1070, 970, 840 cm^{-1}.

Anal. Calcd. for $C_{17}H_{10}Cl_2BrN_4BF_4$: C, 40.19; H, 1.98; N, 11.03; Cl, 13.96; Br, 15.73. Found: C, 40.33; H, 2.06; N, 10.95; Cl, 13.72; Br, 15.34.

1-*p*-Chlorophenyl-3-*p*-bromophenyl-6-morpholino-v-triazolo[1,5-*b*]pyridazinium Fluoborate (**6**).

A mixture of fluoborate salt **5c** (0.25 g, 0.5 mmole), absolute acetonitrile (4 ml) and morpholine (1 ml) was stirred at room temperature for 3 hours. The reaction mixture was then evaporated, and the residue was treated with ethanol. Crystals separated, which were filtered off and recrystallized from acetonitrile-ether to give 0.2 g (71%) of product, mp 229-231°; ir (potassium bromide): 3050, 2960, 2900, 2850, 1600, 1570, 1560, 1500, 1480, 1440, 1260, 1070, 1000, 830 cm^{-1}; ^{1}H nmr (deuterioacetonitrile): δ 8.52 (1H, d, J = 10.25 Hz, 7-H), 7.66 (1H, d, 8-H), 7.98 and 7.70 (4H, AA'BB', 4-chlorophenyl), 7.88 (4H, m, 4-bromophenyl), 3.70 (8H, m, H-morpholine).

Anal. Calcd. for $C_{21}H_{18}ClBrN_5OBF_4$: C, 45.15; H, 3.25; N, 12.45; Cl, 6.35; Br, 14.31. Found: C, 45.34; H, 3.14; N, 12.31; Cl, 6.52; Br, 14.10.

Reaction of **5a** and **5b** with Morpholine.

A mixture of the appropriate triazolopyridazinium salt **5** (1 mmole), acetonitrile (5 ml) and morpholine (0.17 g, 2 mmoles) was stirred at room temperature. A solution was formed first followed by precipitation of a crystalline solid which was filtered off, nmr analysis revealed the presence of two components, **9** and **10**, respectively. The major product could be obtained by successive recrystallizations from ethanol. Reaction of **5a** yielded a mixture (0.23 g) of **9a** and **10a** in a ratio of 3:2, whereas **5b** gave a mixture (0.38 g, 84%) of **9b** and **10b** in a ratio of 1:10.

2-*p*-Bromophenyl-4-(β-cyano-β-morpholinoethyl)-5-methyl-v-triazole (**9a**).

The recrystallizations of the crude product obtained from **5a** from ethanol afforded 0.08 g (21%) of pure **9a**, mp 165-168°; ir (potassium bromide): 2950, 2860, 2840, 2830, 1580, 1500, 1480, 1450, 1410, 1340, 1250, 1120, 1070, 1000, 950, 830 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.8 (4H, m, 4-bromophenyl), 3.95 (1H, t, J = 7.7 Hz, CH), 3.75 (4H, m, morpholine-H), 3.12 (2H, d, CH_2), 2.7 (4H, m, morpholine-H), 2.33 (3H, s, CH_3).

Anal. Calcd. for $C_{16}H_{18}BrN_5O$: C, 51.07; H, 4.82; N, 18.61. Found: C, 51.00; H, 5.06; N, 18.57.

2-*p*-Bromophenyl-5-*p*-chlorophenyl-4-morpholinoethenyl-v-triazole (**10b**).

Recrystallization of the crude product obtained from **5b** from ethanol afforded 0.30 g (67%) of **10b**, mp 161-164°; ir (potassium bromide): 3000, 2950, 2920, 2940, 2840, 1640, 1590, 1480, 1450, 1380, 1340, 1310, 1260, 1200, 1160, 1120, 1090, 1010, 960, 940, 820 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 9.0 and 7.45 (4H, AA'BB', 4-chlorophenyl), 7.75 and 7.45 (4H, AA'BB', 4-bromophenyl), 7.11 (1H, d, olefin-H_A), 5.3 (1H, d, J = 13.8 Hz, olefin-H_B), 3.75 (4H, m, morpholine-H), 3.1 (4H, m, morpholine-H).

Anal. Calcd. for $C_{20}H_{18}ClBrN_4O$: C, 53.89; H, 4.07; N, 12.57; Cl, 7.95; Br, 17.93. Found: C, 53.67; H, 4.33; N, 12.60; Cl, 8.15; Br, 18.04.

2-*p*-Bromophenyl-5-methylmorpholinoethenyl-v-triazole (**10a**).

A solution of **5a** (0.19 g, 0.5 mmole) in acetonitrile was added to a solution of sodium morpholide in absolute tetrahydrofurane (prepared from 0.5 mole of sodium hydride and an equivalent amount of morpholine in tetrahydrofuran). The mixture was stirred for 30 minutes. Water was added, and the precipitated product was filtered off. Recrystallization from ethanol yielded 0.09 g of pure **10a**, mp 122-128°; ir (potassium bromide): 2920, 2800, 1640, 1580, 1490, 1440, 1380, 1340, 1200, 1150, 1100, 1010, 950, 920, 810 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.7 (4H, m, 4-bromophenyl), 6.95 (1H, d, J = 13.9 Hz, olefin-H_A), 5.20 (1H, d, olefin-H_B), 3.75 (4H, m, morpholine-H), 3.10 (4H, m, morpholine-H), 2.30 (3H, s, CH_3).

Anal. Calcd. for $C_{15}H_{17}BrN_4O$: C, 51.59; H, 4.92; N, 16.04. Found: C, 51.48; H, 4.80; N, 15.89.

Preparation of v-Triazolylenethers (**11**).

To a solution of triazolopyridazinium salt **5** (1 mmole) in methanol (4 ml), 2% sodium methoxide solution (2 mmoles) was added dropwise with stirring. A colourless solid precipitated which was filtered off and recrystallized from the given solvent.

2-*p*-Bromophenyl-4-methoxyethenyl-5-methyl-v-triazole (**11a**).

This compound was prepared according to the above procedure starting from **5a** to give 0.21 g (72%, from methanol) of product, mp 82-83°; ir (potassium bromide): 3090, 3050, 2950, 1650, 1580, 1490, 1320, 1200, 1160, 960, 930, 820 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.9 and 7.55 (4H, m, 4-chlorophenyl), 7.30 (1H, d, J = 13 Hz, olefin-H_A), 5.72 (1H, d, olefin-H_B), 3.71 (3H, s, OCH_3), 2.33 (3H, s, CH_3).

Anal. Calcd. for $C_{12}H_{12}BrN_3O$: C, 49.00; H, 4.11; N, 14.28; Br, 27.16. Found: C, 49.29; H, 4.09; N, 14.36; Br, 27.21.

2-*p*-Bromophenyl-5-*p*-chlorophenyl-4-methoxyethenyl-v-triazole (**11b**).

This compound was prepared from **5b** to give 0.32 g (82%, from methanol-chloroform) of product, mp 100-103°; ir (potassium bromide): 3070, 3000, 2920, 2830, 1640, 1580, 1490, 1200, 1150, 1080, 1010, 970, 930, 850, 830, 820 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 8.0 and 7.55 (4H, m, 4-bromophenyl), 7.65 and 7.42 (4H, m, 4-chlorophenyl), 7.37 (1H, d, olefin-H_A), 5.80 (1H, d, J = 12.7 Hz, olefin-H_B), 3.71 (3H, s, OCH_3).

Anal. Calcd. for $C_{17}H_{13}ClBrN_3O$: C, 52.26; H, 3.35; N, 10.75; Cl, 9.07; Br, 21.03. Found: C, 52.03; H, 3.16; N, 10.73; Cl, 9.18; Br, 20.74.

Preparation of v-Triazolylenethioethers **12**.

To a suspension of the corresponding triazolopyridazinium salt **5** (0.5 mmole) in ethanol (1 ml), a solution of benzylmercaptan (1 mmole) and potassium hydroxide (1 mmole) in ethanol was added dropwise at a temperature of 5-10°. Upon the addition of

the reagent, a solution was first formed, followed by separation of a precipitate. The product was filtered off and recrystallized from the given solvent.

4-Benzylthioethenyl-2-*p*-bromophenyl-5-methyl-v-triazole (**12a**).

This compound was obtained from **5a** to give 0.18 g (95%, from ethanol) of product, mp 72-74°; ir (potassium bromide): 3010, 2920, 1610, 1580, 1480, 1450, 1330, 950, 830, 790, 700 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.86 and 7.57 (4H, m, 4-bromophenyl), 7.3 (5H, m, phenyl), 7.02 (1H, d, olefin-H_A), 6.42 (1H, d, J = 15.6 Hz, olefin-H_B), 4.0 (2H, s, CH_2-H), 2.29 (3H, s, CH_3).

Anal. Calcd. for $C_{18}H_{16}BrN_3S$: C, 55.96; H, 4.17; N, 10.88; S, 8.30; Br, 20.69. Found: C, 55.97; H, 4.48; N, 10.81; S, 8.31; Br, 21.34.

4-Benzylthioethenyl-2-*p*-bromophenyl-5-*p*-chlorophenyl-v-triazole (**12a**).

This compound was obtained from **5b** to give 0.22 g (90%, from ethanol-chloroform) of product, mp 94-96°; ^1H nmr (deuteriochloroform): δ 7.95 and 7.55 (4H, m, 4-bromophenyl), 7.50 (9H, m, 4-chlorophenyl and phenyl), 7.25 (1H, d, olefin-H_A), 6.43 (d, 1H, J = 15.35 Hz, olefin-H_B), 4.01 (2H, s, CH_2-H).

Anal. Calcd. for $C_{23}H_{17}ClBrN_3S$: C, 57.21; H, 3.55; N, 8.70. Found: C, 57.48; H, 3.44; N, 8.42.

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