to accommodate such situations, the correlation of Szafraniec between $^1J_{PF}$ and σ^+ and that of Pomerantz et al. between $^1J_{PN}$ and σ^- values seems reasonable. In contrast, the $^1J_{PC}$ coupling is expected to be determined primarily by the contact term. Consequently, it was of interest to see if either resonance or field parameters individually would provide empirical correlations with $^1J_{PC}$ coupling constants. The results of such attempts are also contained in Table VI. From these it is apparent that for the one-bond coupling constants correlations for para substituents using the resonance parameter alone are nearly as good as those employing both resonance and field parameters. For meta substituents, there is a definite lack of correlation using the individual parameter sets, except in the case of series 1, for which the correlation with the field parameter is equivalent to that employing both. Thus, in these systems, the resonance parameters alone apparently provide a nearly adequate reflection of trends in the contact term for para-substituted compounds, but not, of course, for the meta series.

Acknowledgment. We thank Drs. R. Bright and C. W. Allen of the Chemistry Department at the University of Vermont for obtaining the ^{31}P NMR spectra of the compounds in series 2. We also thank J. L. Pflug of the F. J. Seiler Research Laboratory for help in obtaining the ^{31}P NMR spectra of the compounds in series 1.

Supplementary Material Available: ^1H, ^{13}C, and ^{31}P NMR data, infrared absorptions, and mass spectral fragmentation patterns for four representative compounds from each series (5 pages). Ordering information is given on any current masthead page.

Selective Ring Openings of Isomeric Fused Thiazolium Salts with Nucleophiles[1]

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Different types of reactions have been found with isomeric tricyclic fused thiazolium salts for their interactions with secondary amines. Thus, the angularly fused quinolinium salt **7** gave rise to a stable pseudobase **8**; the related angular isoquinolinium system **9** led to opening of the thiazole ring and enamine **10** was formed; and the linear system **6** underwent opening of the pyridine moiety and gave the aldehyde compound **16**. The reactions were interpreted on FMO theory; the CNDO/2 calculation supported the qualitative picture based on the "annelation effect".

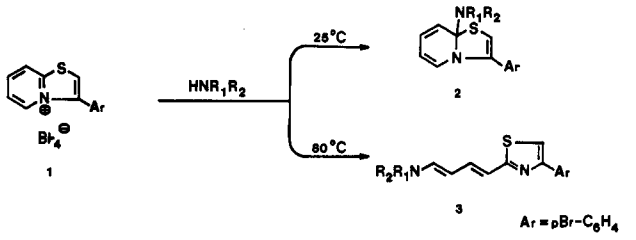
Recently we reported[2] that the reaction of thiazolo[3,2-*a*]pyridinium salt **1** with a secondary amine results in both a pseudobase **2** and thiazolyl dieneamine **3** depending on the reaction conditions (Scheme I). As a consequence of these findings, the question of how the differently annelated benzologues of **1** (i.e., **6**, **7**, and **9**) behave in similar reactions is of interest. In the literature, only a few examples of nucleophilic reactions of tricyclic fused thiazolium salts have been described.[3-5]

Two of the possible benzologue systems, i.e. the angularly fused thiazoloisoquinolinium and quinolinium salts (**7**, **9**), have been reported[5] whereas the linearly fused thiazolo[3,2-*b*]isoquinolinium system has not yet been synthesized.

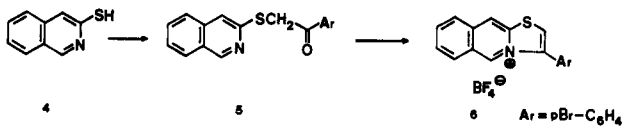
Preparation of this latter linearly fused system (**6**) was accomplished by application of the method described for the angularly fused isomers.[5] Thus, 3-mercaptoisoquinoline (**4**) was treated with *p*-bromophenacyl bromide, and the resulting sulfide (**5**) was cyclized by using concentrated sulfuric acid. The new ring system as well as the earlier known angular ones were transferred to stable fluoborate salts (**6**, **7**, **9**) (Scheme II).

Reaction of 1-(*p*-bromophenyl)thiazolo[3,2-*a*]-quinolinium fluoborate (**7**) with morpholine at room temperature gave stable pseudobase **8** that could be converted to the starting thiazolium salt **7** by treatment with acid

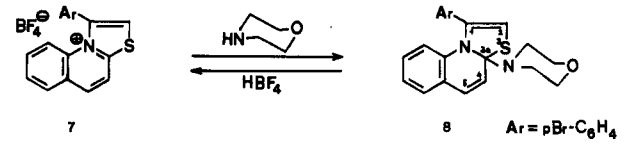
Scheme I



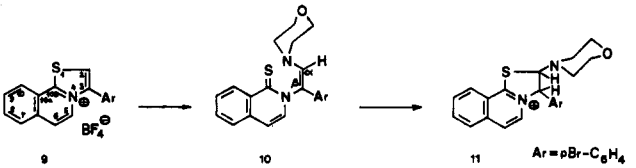
Scheme II



Scheme III



Scheme IV



(Scheme III). Structure **8** is based on ^1H NMR data: an alternative structure having a 5-morpholino substituent

(1) Fused Azolium Salts. 10. Part 9: Messmer, A.; Hajós, Gy.; Gelléri, A.; Radics, L. *Tetrahedron* **1986**, *42*, 5415.
(2) Hajós, Gy.; Messmer, A. *J. Heterocycl. Chem.* **1984**, *21*, 809.
(3) Singh, H.; Lal, K. *J. Chem. Soc., Perkins Trans. 1* **1972**, 1799.
(4) Molina, P.; Arques, A.; Cartagena, I.; Noguera, J. A.; Valcarcel, V. *J. Heterocycl. Chem.* **1983**, *20*, 983.
(5) Bradsher, C. K.; Lohr, D. F. *J. Heterocycl. Chem.* **1967**, *4*, 71.

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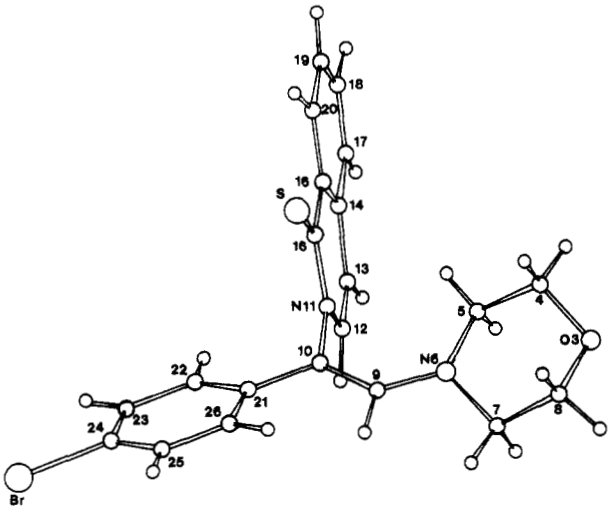


Figure 1. 10 obtained by X-ray analysis. An arbitrary numbering was used for C, N, and O atoms.

instead of 3a would not be consistent with the chemical shifts of the doublet pair assigned to H-4 and H-5 in the ^{1}H NMR spectrum. The fact that pseudobase 8 and the starting azolium salt 7 give the same fragmentation in the mass spectrum verifies the ring-closed structure of 8 and excludes a possible ring opening (e.g., a process analogous to formation of 10 from 9). Interestingly, even at elevated temperatures, formation of pseudobase 8 only was observed.

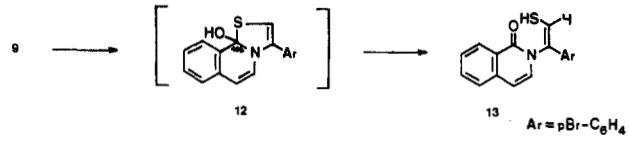
A different reactivity was found in the case of the other angularly fused isomer 9. This thiazolium salt did not react with morpholine at room temperature. At higher temperatures (in boiling morpholine), however, a very rapid change took place and ring-opened product 10 could be isolated in good yield. The structure of this compound was supported by its ^{13}C NMR spectrum; an unambiguous proof, however, could only be given by crystal structure analysis (Figure 1). This finding shows that carbon-2 was attacked by the reagent followed by opening of the thiazole ring yielding isoquinolinethione derivative 10 (Scheme IV).

When compound 10 was treated with acid, ring closure to dihydro compound 11 occurred. This can be explained by the enamine character of 10: protonation takes place at the β-carbon atom of the enamine chain followed by a nucleophilic addition of sulfur to the α-carbon atom. The structure of 11—which can also be regarded as a formal addition product of morpholine to the parent cation 9—was proved by its ^{1}H NMR spectrum where protons H-2 and H-3 showed two doublets at 6.6 and 5.85 ppm with a coupling constant of 2.5 Hz.

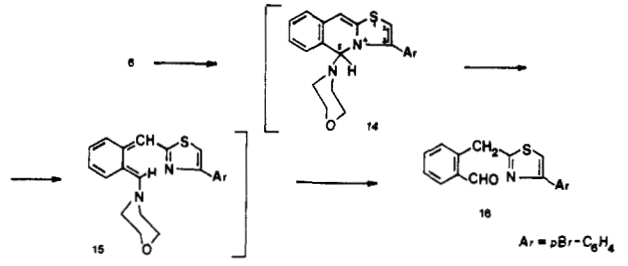
While formation of pseudobase 8 from the thiazolium salt 7 is strongly remeniscent of the case of bicyclic system 1 (formation of 2), the observed reactivity of the angularly fused tricyclic salt 9—i.e., predominance of nucleophilic attack at C-2—is essentially different from the behavior of system 1: if 9 reacted in a similar manner as system 1, attack of the nucleophile at positions C-5 and C-10b would be expected. Formation of the 5-substituted pseudobase, however, would involve destruction of the aromatic sextet in the benzene ring and is therefore not probable. The lack of attack at C-10b can, on the other hand, be ascribed to steric hindrance. This latter supposition, however, implies that attack of smaller nucleophiles can be expected at position 10b.

In accordance with this consideration, thiazoloisoquinolinium salt 9, when treated with aqueous tetrabutylammonium hydroxide, gave rise to isocarbostyril derivative 13, formation of which can only be interpreted

Scheme V



Scheme VI



by supposing formation of intermediate 12 (10b-substituted pseudobase). The structure of the ring-opened product 13 was proved by ^{1}H NMR and mass spectrometry (Scheme V).

Behavior of the linearly fused thiazoloisoquinolinium salt 6 in the presence of morpholine was found to be different from that of both angularly fused isomers 7 and 9. Treatment of 3-(*p*-bromophenyl)thiazolo[3,2-*b*]isoquinolinium fluoborate (6) with morpholine in acetonitrile solution followed by addition of water to the reaction mixture resulted in formation of aldehyde derivative 16. The same product was obtained with the reaction of 6 with tetramethylammonium hydroxide. In this case the attack of the nucleophile took place evidently at C-5. A possible retroelectrocyclization of the supposed intermediate 14 and reaction of the opened species 15 with water could lead to product 16. Some similarity can be recognized between formation of 16 from 6 and that of 3 from 1. Obviously, however, the the supposed intermediate 15, which can be regarded as the "benzologue" of dieneamine 3, is rather unstable because of its quinonoid character and is therefore easily stabilized by water addition and hydrolysis (Scheme VI).

Comparison of reactivities of the bicyclic thiazolium salt 1 and the linear and angular tricyclic benzologues 6, 7, and 9 shows that the site of attack of the nucleophile can essentially be changed by alteration of the type of annelation. To understand these significant changes with the different annelations and the observed high selectivities, we decided—as in our earlier studies[1]—to apply the frontier molecular orbital theory. Calculation of the electronic distribution was carried out for the four heteroaromatic cations by CNDO/2 method.[6] In the case of the tricyclic systems (6, 7, 9), a geometry containing the thiazolopyridinium moiety of known bonds and angles[7] and an annelated regular hexagon was assumed. Table I contains the c_{LUMO} coefficients and q_{NET} charges for the four positions adjacent to the heteroatoms.

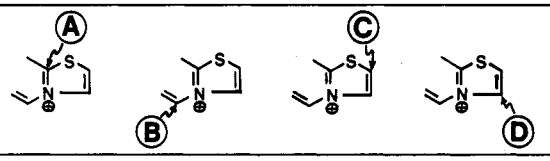
In Table I, data pairs containing considerably higher values than the other figures in that row and therefore representing a preferred position for the nucleophilic attack are marked by asterisks. (Morpholine can be regarded as a medium-soft nucleophile,[8] and therefore both c_{LUMO} and q_{NET} values are important.) Evaluation of Table I

(6) Pople, J. A.; Santry, D. P.; Segel, G. A. *J. Chem. Phys.* **1960**, *43*, S129.

(7) Sasvári, K.; Párkányi, L; Hajós, Gy.; Hess H.; Schwartz, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1229.

(8) Ho, Tse-Lok *Hard and Soft Acids and Bases Principle in Organic Chemistry*; Academic: New York, 1977; p 6.

Table I. c_{LUMO} Coefficients and q_{NET} Positive Charges of the Four Positions Adjacent to the Heteroatoms Calculated by CNDO/II[a]



1	0.44*	0.41*	0.29	0.10
	(0.16)	(0.12)	(0.03)	(0.04)
9	0.57*	0.17	0.24*	0.06
	(0.17)	(0.08)	(0.02)	(0.04)
6	0.15	0.56*	0.25	0.08
	(0.13)	(0.13)	(0.03)	(0.03)
7	0.47*	0.19	0.22	0.05
	(0.18)	(0.14)	(0.01)	(0.05)

[a] Large values are c_{LUMO}, and q_{NET} positive charges are in parentheses. Positions that can be predicted as probable targets of a nucleophilic attack are marked by asterisks. Aryl substituents were replaced by hydrogen in each case of calculation. Letters A–D stand for the four different types of attack.

shows that our experimental findings are in rather good agreement with these theoretical predictions:

(i) Bicyclic system 1: Attacks at centers A and B are equally probable acording to these data and, indeed, attacks at these points were found experimentally.

(ii) Thiazolo[2,3-*a*]isoquinolinium system 9: Attack of type A is highly preferred by the data and is, in fact, realized in the case of the small hydroxyl ion. With a larger nucleophile, however, attack at only the second probable—and sterically not hindered—position was found.

(iii) Linearly fused thiazolo[3,2-*b*]isoquinolinium system 6: Attack B can unambiguously be predicted by the figures; the experiments show that only this attack is realized.

(iv) Thiazolo[3,2-*a*]quinolinium system 7: Nucleophilic attack was observed only at site A having the highest c_{LUMO} coefficient (i.e., there is no steric hindrance).

Our experimental findings and theoretical considerations show that alteration of the annelation of these fused thiazolium systems involves important changes in the heteroaromatic electronic distribution and leads to dramatic changes in the reactivity with nucleophiles. In our previous studies we showed [1,9] that this annelation effect of fused heteroaromatic systems could be sufficiently explained by the following consideration: among isomers, those containing a greater number of isolated benzene-like π sextets—formulated by circles standing exactly for six π electrons—are energetically preferred. (This is an extension of Clar's principle[11]—elaborated originally for carbocycles—to heteroaromatic systems.)

The above experimental results also showed that attack of the nucleophile was found to take place at those centers (e.g., 9-A, 6-B, and 7-A; see Table I) whereby the π sextet of the benzene ring is retained. Both this qualitative consideration and the semiempirical calculation as shown above seem to support this "heteroaromatic annelation effect".

Experimental Section

Melting points were determined on a Büchi apparatus and are uncorrected. IR spectra were recorded on a Unicam SP 200 and UV spectra on a Unicam SP 800 instrument. ^{1}H NMR spectra (60 MHz) were obtained on a Varian EMX-360 spectrometer, the 100-MHz ^{1}H NMR spectra and the ^{13}C NMR spectra were recorded on a Varian XL-100 instrument. Mass spectra were obtained with an AEI MS-902 spectrometer. The quantum chemical calculations were carried out on an IBM 3031 computer.

X-ray Analysis. Crystal data: $C_{21}H_{18}BrN_2OS$, M_r 426.4; a = 8.466 (1), b = 12.316 (1), c = 18.516 (2) Å; β = 99.92 (1)°; V = 1901.8 (6) Å^3; D_x = 1.489 g cm^{-3}; μ(Cu K$_\alpha$, λ = 1.5418 Å) = 41 cm^{-1}; z = 4; space group $P2_1/c$.

A total of 3782 unique reflections with nonzero intensities were collected on an Enraf-Nonius CAD4 computer-controlled diffractometer, with θ–2θ scan in the $3 < 2\theta < 150°$ range (approximate crystal size 0.08 × 0.12 × 0.20 mm). The structure was determined by direct methods and was refined by full-matrix least squares. Hydrogen atoms were generated from assumed geometries and were refined in the last two least-squares cycles with their isotropic temperature factor fixed at 4.0 Å^2. The final R values are 0.043 for 3576 observations ($I > 2\sigma(I)$, where $\sigma(I)$ is the standard deviation of the intensity, based on counting statistics) and 0.052 for all reflections. Atomic coordinates are given in the microfilm supplement.[12] No unusual bond distances and angles were observed.

1-(*p*-Bromophenyl)thiazolo[3,2-*a*]quinolinium Fluoborate (7). This compound was prepared according to the procedure of Bradsher et al.[5] described for the corresponding perchlorate salt. The fluoborate derivative was obtained from the reaction mixture by addition of 40% fluoboric acid in 67% yield; mp 210–211 °C. Anal. Calcd for $C_{17}H_{11}BBrF_4NS$: C, 47.70; H, 2.59; N, 3.27; S, 7.49. Found: C, 47.52; H, 2.48; N, 3.11; S, 7.29.

3-(*p*-Bromophenyl)thiazolo[2,3-*a*]isoquinolinium Fluoborate (9). The reaction mixture obtained as described by Bradsher et al.[5] for the analogous perchlorate salt was treated with 40% fluoboric acid to give fluoroborate salt in 70% yield; mp 247–248 °C. Anal. Calcd for $C_{17}H_{11}BBrF_4NS$: C, 47.70; H, 2.59; N, 3.27; S, 7.29. Found: C, 47.59; H, 2.39; N, 3.05; S, 7.42.

3-[(*p*-Bromophenacyl)thio]isoquinoline (5). To a solution of 3-mercaptoisoquinoline[10] (0.5 g, 3.1 mmol) in glacial acetic acid (5 mL) was added *p*-bromophenacyl bromide (0.95 g, 3.4 mmol), and the mixture was stirred. Within some minutes colorless crystals separated. After a period of 1 h, 10 mL of water was added to the reaction mixture and the product was filtered and recrystallized from methanol to give 0.56 g (52%) of colorless crystals: mp 90–92 °C; NMR (deuteriochloroform) δ 9.0 (s, 1 H, H-1), 8.0–7.2 (m, 5 H, H-Ar), 4.7 (s, 2 H, CH_2). Anal. Calcd for $C_{17}H_{12}BrNOS$: C, 56.99; H, 3.38; N, 3.91; S, 8.95. Found: C, 56.70; H, 3.21; N, 3.91; S, 9.02.

3-(*p*-Bromophenyl)thiazolo[3,2-*b*]isoquinolinium Fluoborate (6). A solution of phenacylthio compound 5 (1.0 g, 2.8 mmol) in 10 mL of sulfuric acid was allowed to stand at room temperature for 24 h and was then poured onto a mixture of 50 g of ice water and 5 mL of 40% fluoboric acid. The resulting pale yelow precipitate was collected and recrystallized from acetonitrile–ether to give 0.8 g (68%) of compound 6: mp 265–267 °C; NMR (dimethyl-d_6 sulfoxide) δ 10.1 (s, 1 H, H-5), 9.6 (s, 1 H, H-10), 8.8–7.8 (m, 9 H, H-Ar). Anal. Calcd for $C_{17}H_{11}BBrF_4NS$: C, 47.70; H, 2.59; N, 3.27. Found: C, 47.61; H, 2.82;, N, 2.99.

1-(*p*-Bromophenyl)-3a,10-dihydro-3a-morpholinothiazolo[3,2-*a*]quinoline (8). A mixture of 0.5 g (1.2 mmol) of fluoborate salt 7 and 5 mL of morpholine was stirred at room temperature for 30 min. The starting suspension became a clear solution from which deep yellow solid deposited. Water (30 mL) was added to the reacton mixture, and the precipitate was filtered and recrystallized from dimethylformamide to give 0.36 g (72%) of pseudobase 8; mp 217–218 °C; ^{1}H NMR (dimethyl-d_6 sulfoxide) δ 8.7 (s, 1 H, H-thiazolyl), 8.6 (d, 1 H, H-5), 8.05 (d, 1 H, H-4), 7.7–7.4 (m, 4 H, H-Ar), 7.3 and 6.8 (two d, 4 H, H-*p*-bromophenyl), 3.8–3.4 (m, 8 H, H-morpholine); MS, m/z 427 (3%, M$^+$), 341 (59%, $C_{17}H_{11}BrNS^+$), 260 (16%), 161 (32%), 128 (56%), 87 (66%, morpholine). The same fragments—except m/z 427 and 87—were shown by the mass spectrum of thiazolium salt 7. Anal. Calcd for $C_{21}H_{19}BrN_2OS$: C, 59.02; H, 4.48; N, 6.56; S, 7.50. Found: C, 58.75; H, 4.28; N, 6.38; S, 7.22.

2-[α-(*p*-Bromophenyl)-β-morpholinoethenyl]isoquinoline-1(2*H*)-thione (10). A solution of thiazolium salt 9 (0.5 g, 1.2 mmol) in 5 mL of morpholine was refluxed for 3 min

(9) Hajós, Gy.; Messmer, A.; Neszmélyi, A.; Párkányi, L. *J. Org. Chem.* **1984**, *49*, 3199.
(10) Albert, A.; Barlin, R. *J. Chem. Soc.* **1959**, 384.
(11) Clar, E. *The Aromatic Sextet*; Wiley: New York, 1972.

(12) See paragraph at the end of paper regarding supplementary material.

and was treated after cooling with 50 mL of water. The precipitate was filtered and recrystallized from acetonitrile to give 0.34 g (69%) of product: mp 188–190 °C; ^{1}H NMR (deuteriochloroform) δ 9.1 (m, 1 H, H-8), 7.8–6.8 (m, 9 H, H-Ar), 6.6 (s, 1 H, H-β), 3.8–2.9 (m, 8 H, H-morpholine); ^{13}C NMR (deuteriochloroform, doublet signals) δ 136.29, 134.25, 132.82, 132.76, 131.69 (2 C), 128.69, 126.87, 124.97 (2 C), 111.96, 66.72 (2C), 49.66 (2C); MS, *m/z* 427 (6%, M^+), 341 (100%, $C_{17}H_{11}BrNS^+$), 266 (5%), 260 (12%), 161 (6%), 128 (13%) (no peak at *m/z* 87). Anal. Calcd for $C_{21}H_{19}BrN_2OS$: C, 59.02; H, 4.48; N, 6.56; S, 7.50. Found: C, 58.80; H, 4.37; N, 6.38; S, 7.24.

3-(*p*-Bromophenyl)-2,3-dihydro-2-morpholinothiazolo-[2,3-*a*]isoquinolinium Fluoborate (11). To a suspension of compound **10** (0.5 g, 1.2 mmol) in 5 mL of acetonitrile was added 1 mL of 40% fluoboric acid with stirring. On addition of water, colorless crystals separated from the mixture that were recrystallized from acetonitrile–ether to give 0.43 g (71%) of product: mp 212–214 °C; ^{1}H NMR (trifluoroacetic acid) δ 9.5–7.2 (m, 10 H, H-Ar), 6.9 and 5.85 (two d, 2 H, H-2 and H-3, $J_{2,3}$ = 2.5 Hz), 3.9–2.4 (m, 8 H, H-morpholine). Anal. Calcd for $C_{21}H_{20}BBrF_4N_2OS$: C, 48.96; H, 3.91; N, 5.44; S, 6.22. Found: C, 48.74; H, 3.81; N, 5.38; S, 6.01.

2-[α-(*p*-Bromophenyl)-β-mercaptoethenyl]isoquinolin-1-(2*H*)-one (13). A mixture of thiazolium salt **9** (0.5 g, 1.2 mmol), 5 mL of acetonitrile, and 1 mL of 10% aqueous tetramethylammonium hydroxide solution was stirred for 24 h at room temperature. During this period, a colorless solution was formed first and then a slow precipitation of a white solid commenced. After filtration and recrystallization from nitromethane, 0.25 g (58%) of product was obtained: mp 210–212 °C; ^{1}H NMR (deuteriochloroform) δ 8.6 (m, 1 H, H-8), 7.9–7.1 (m, 8 H, H-Ar), 6.9 and 6.5 (two d, 2 H, H-3 and H-4, $J_{3,4}$ = 8 Hz); MS, *m/z* 357 (3%, M^+), 340 (2%), 325.0028 ($C_{17}H_{11}NOBr^+$ (M - SH)$^+$, 100). Anal. Calcd for $C_{17}H_{12}BrNOS$: C, 56.99; H, 3.38; N, 3.92; S, 8.98. Found: C, 57.01; H, 3.49; N, 3.84; S, 8.67.

α-[4-(*p*-Bromophenyl)thiazol-2-yl]-*o*-tolualdehyde (16). A mixture of thiazolium salt **6** (0.5 g, 1.2 mmol), 5 mL of acetonitrile, and 1 mL of morpholine was stirred for 1 h at room temperature, and the resulting solution was poured onto 40 g of ice water. The oily precipitate that began to crystallize slowly was filtered and was eluted on silica by ethyl acetate to give 0.26 g (62%) of product **16** mp 157–158 °C; ^{1}H NMR (deuteriochloroform) δ 10.3 (s, 1 H, H-aldehyde), 8.0–7.2 (m, 9 H, H-Ar), 4.8 (s, 2 H, CH_2). Anal. Calcd for $C_{17}H_{12}BrNOS$: C, 56.99; H, 3.38; N, 3.91; S, 8.95. Found: C, 56.85; H, 3.44; N, 3.62; S, 8.80.

Acknowledgment. Thanks are due to Dr. A. Neszmélyi for the NMR spectra and for the valuable discussions.

Registry No. **4**, 98589-68-5; **5**, 107454-06-8; **6**, 107454-08-0; **7**, 107454-02-4; **8**, 107454-03-5; **9**, 107454-04-6; **10**, 107454-05-7; **11**, 107454-11-5; **13**, 107454-09-1; **16**, 107454-12-6; *p*-bromophenacyl bromide, 99-73-0; morpholine, 110-91-8.

Supplementary Material Available: Listing of atomic coordinates and their esd values (1 page). Ordering information is given on any current masthead page.

Organoselenium-Induced Cyclization of Olefinic Imidates and Amides. Selective Synthesis of Lactams or Iminolactones

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Lactams were formed selectively by the cyclization of olefinic imidates through the addition of a phenylseleno group to the double bond. Similar cyclization of olefinic amides, on the other hand, afforded either iminolactones or lactams depending on the structure of alkenyl moiety in the amides. The structure of lactams thus produced was confirmed by their lithium aluminum hydride reduction to nitrogen heterocycles. Iminolactones bearing a chloroalkyl substituent on the imino nitrogen were utilized in the synthesis of eight- or nine-membered cyclic compounds containing both oxygen and nitrogen atoms in the ring by a novel ring-enlargement reaction.

Numerous studies have reported that the reactions of olefinic alcohols or acids with phenylselenenyl halides afford cyclic ethers[1] or lactones[2] through the addition of a phenylseleno group to the double bond and subsequent cyclization by the carbon–oxygen bond formation. These reactions have been utilized in the synthesis of natural products and related compounds.[3] Organoselenium-induced cyclization of *N*-alkenylamine derivatives has also been reported to produce pyrrolidine or piperidine derivatives[4] by the formation of a carbon–nitrogen bond. In the case of olefinic amides, we found that different type reactions proceed depending on the structure of alkenyl moiety.[5] Thus, iminolactones were produced from 4-

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