An intramolecular bromonium to thiiranium ion rearrangement

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and *N*-phenylbenzimidoyl fluoride (0.01 mol) were boiled in ethylene chloride as described for pyridine 1-oxide. 3-Picoline 1-oxide hydrofluoride separated (identified by its giving a positive color test for F_3^-[8] and by its giving 3-picoline 1-oxide on treatment with alkali). Again no ring-fluorinated product was detected by GLC. Chromatography on Sephadex LH 20 as before gave a mixture of 2- and 6-(*N*-benzoylanilino)-3-picoline [1.001 g (35%). Anal. Calcd for $C_{19}H_{16}N_2O$: N, 9.59. Found: N, 9.72] and benzanilide (0.493 g, 25%). The mixture of isomers was resolved by TLC on silica gel with benzene/ethanol (5:1 v/v) as the developer. The products were identical with authentic samples.[7] By use of a densitometer to scan the TLC plates, the 2,3-/2,5-isomer ratio was found to be approximately 1:40 (±15%).

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Registry No. 1, 626-60-8; 2 (Ar = Ph), 20107-78-2; 2 (Ar = 2-$CH_3C_6H_4$), 87281-82-1; 2 (Ar = 3-$CH_3C_6H_4$), 87281-83-2; 2 (Ar = 4-$CH_3C_6H_4$), 56969-75-6; 2 (Ar = 2,4-$(CH_3)_2C_6H_3$), 87281-84-3; 2 (Ar = 3,5-$(CH_3)_2C_6H_3$), 87281-85-4; 2 (Ar = 2-$OCH_3C_6H_4$), 87319-90-2; 2 (Ar = 3-$OCH_3C_6H_4$), 87281-86-5; 2 (Ar = 4-$OCH_3C_6H_4$), 56969-76-7; 2 (Ar = 2,4-$(OMe)_2C_6H_3$), 87308-16-5; 2 (Ar = 3,5-$(OMe)_2C_6H_3$), 87281-87-6; 2 (Ar = 2-ClC_6H_4), 87281-88-7; 2 (Ar = 3-ClC_6H_4), 87281-89-8; 2 (Ar = 2,4-$Cl_2C_6H_3$), 87281-90-1; 2 (Ar = 3,4-$Cl_2C_6H_3$), 87281-91-2; 2 (Ar = 2-$NO_2C_6H_4$), 87281-92-3; 2 (Ar = 3-$NO_2C_6H_4$), 87281-93-4; 3 (Ar = 3,4-$Cl_2C_6H_3$), 6043-42-1; 3 (Ar = Ph), 93-98-1; 3 (Ar = 2-$CH_3C_6H_4$), 7055-03-0; 3 (Ar = 3-$CH_3C_6H_4$), 23099-05-0; 3 (Ar = 4-$CH_3C_6H_4$), 6833-18-7; 3 (Ar = 2,4-$(CH_3)_2C_6H_3$), 5180-83-6; 3 (Ar = 2-$OCH_3C_6H_4$), 6833-21-2; 3 (Ar = 3-$OCH_3C_6H_4$), 6833-23-4; 3 (Ar = 4-$OCH_3C_6H_4$), 7465-88-5; 3 (Ar = 2,4-$(OMe)_2C_6H_3$), 1718-94-1; 3 (Ar = 3,5-$(OMe)_3C_6H_3$), 87282-04-0; 3 (Ar = 2-ClC_6H_4), 6833-13-2; 3 (Ar = 3-ClC_6H_4), 6832-92-4; 3 (Ar = 2-$NO_2C_6H_4$), 2385-27-5; 3 (Ar = 3-$NO_2C_6H_4$), 2243-73-4; 3 (Ar = 2,4-$(NO_2)_2C_6H_3$), 22978-56-9; 3 (Ar = 3,5-$(NO_2)_2C_6H_3$), 7461-51-0; 3 (Ar = 3,5-$Me_2C_6H_3$), 87282-03-9; 3 (Ar = 2,4-$Cl_2C_6H_3$), 6043-39-6; PhCCl=NPh, 4903-36-0; 2-$CH_3C_6H_4CCl$=NPh, 51619-51-3; 3-$CH_3C_6H_4CCl$=NPh, 87281-94-5; 4-$CH_3C_6H_4CCl$=NPh, 34916-13-7; 2,4-$(CH_3)_2C_6H_3CCl$=NPh, 87281-95-6; 3,5-$(CH_3)_2C_6H_3CCl$=NPh, 87281-96-7; 2-$OCH_3C_6H_4CCl$=NPh, 59386-97-9; 3-$OCH_3C_6H_4CCl$=NPh, 87281-97-8; 4-$OCH_3C_6H_4CCl$=NPh, 38968-72-8; 2,4-$(OMe)_2C_6H_3CCl$=NPh, 87281-98-9; 3,5-$(OMe)_2C_6H_3CCl$=NPh, 87281-99-0; 2-ClC_6H_4CCl=NPh, 59387-00-7; 3-ClC_6H_4CCl=NPh, 55832-04-7; 2,4-$Cl_2C_6H_3CCl$=NPh, 87282-00-6; 3,4-$Cl_2C_6H_3CCl$=NPh, 87282-01-7; 2-$NO_2C_6H_4CCl$=NPh, 57761-80-5; 3-$NO_2C_6H_4CCl$=NPh, 5509-90-0; 2,4-$(NO_2)_2C_6H_3CCl$=NPh, 87282-02-8; 3,5-$(NO_2)_2C_6H_3CCl$=NPh, 29955-47-3; pyridine oxide, 694-59-7.

An Intramolecular Bromonium to Thiiranium Ion Rearrangement

John M. Bland and Charles H. Stammer*

University of Georgia, Chemistry Department, Athens, Georgia 30602

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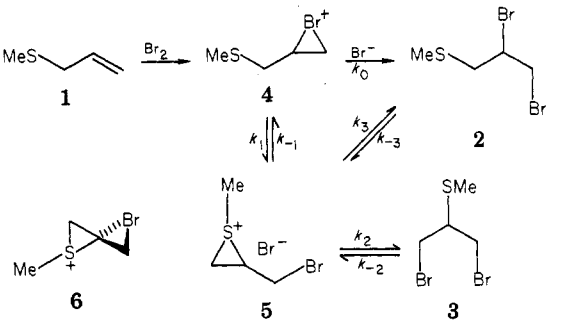
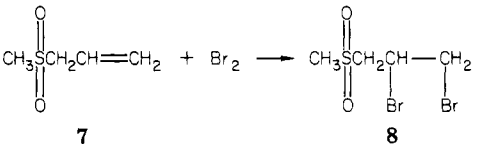
In connection with our synthetic program, we had occasion to carry out the bromination of methyl allyl sulfide (1) at 0 °C in CCl_4 solution with the intention of obtaining the unsymmetrical dibromide 2. It was immediately clear from the ^1H NMR spectrum of the product that 2 was not formed and that the symmetrical structure 3 best accommodated the spectroscopic evidence. A ^{13}C spectrum of the product showed only three peaks (Table I), while four peaks were expected for the unsymmetrical compound 2. When 3 was heated in refluxing $CDCl_3$, four new peaks appeared in the ^{13}C spectrum corresponding to structure 2. The equilibrium mixture (after 5 h) contained approximately 82% of 2 according to direct measurement of the methyl peak heights in the ^{13}C spectrum at room temperature.



The explanation for this behavior must lie in the tremendous ease with which the "mustard" type of structure can form thiiranium ions.[1] The fact that the symmetrical compound 3 is the kinetic product while the expected product 2 is the thermodynamic one requires that an intermediate thiiranium ion (5) be formed directly from the bromonium ion (4). To our knowledge there is no known case that invokes the rapid intramolecular conversion of a bromonium ion into a thiiranium ion. The transition state for such a rearrangement requires a spiro[2.2]pentane structure (6) which has the two three-membered rings in an orthogonal arrangement. This phenomenon (4 ⇌ 5) is, however, required to explain the formation of 3 in this case, because it is not energetically feasible that the thermodynamically more stable product 2 is intermediate in the formation of 3 from 4. Quantitatively speaking, $k_1 > k_0$ and $k_2 > k_3$, but since $K_3 > K_2$, k_{-2} must be considerably greater than k_{-3}. For this reason, at temperatures greater than 25 °C, we expect bromination of 1 to give a mixture of 2 and 3. The rapid opening of the thiirane ring at the primary carbon of 5 giving 3 is consistent with what is known[2] about these reactions in nonpolar solvents such as CCl_4.

Since the proposed mechanism requires participation of the sulfur atom, we investigated bromination of allyl methyl sulfone[3] (7) in which the sulfur atom should be unable to participate in the reaction. Four signals in both the ^1H and ^{13}C NMR spectra of the product indicated that the sole bromo compound formed at room temperature was the unsymmetrical dibromo sulfone 8 (Table II). The



7 8

spectra of 8 were unchanged after a week at ambient temperature, indicating no tendency to rearrange. This result strengthens the proposed hypothesis that a bro-

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(2) See Bolster, J.; Kellog, R. M. *J. Chem. Soc., Chem. Commun.* **1978**, 630 and references therein.

(3) Attempts to use methyl allyl *sulfoxide* led to mixtures containing 2 and 3 formed, apparently, from 1 produced by bromine reduction (see Aida, T.; Furukawa, N.; Oae, S. *Tetrahedron Lett.* **1973**, 3853) of the starting sulfoxide.

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Table I

C	(1) ^{1}H	(1) ^{13}C[a]	(2) ^{1}H	(2) ^{13}C[a]	(3) ^{1}H	(3) ^{13}C[a]
C_1	2.05 (s)	14.1 (q)	2.25 (s)	16.6 (q)	2.25 (s)	15.1 (q)
C_2	3.15 (d)	36.7 (t)	3.15 (d of d)	40.3 (t)	3.2–2.9 (m)	49.1 (d)
C_3	6.1–5.6 (m)	133.9 (d)	4.5–4.15 (m)	50.5 (d)	3.75 (d of d)	33.9 (t)
C_4	5.25–5.0 (m)	116.7 (t)	4.0–3.7 (m)	36.0 (t)		

[a] Multiplicity (s, d, t, q) as determined from off-resonance decoupled spectra.

Table II

C	(7) ^{1}H	(7) ^{13}C[a]	(8) ^{1}H	(8) ^{13}C[a]
C_1	2.90 (s)	38.7 (q)	3.1 (s)	42.8 (q)
C_2	3.80 (d)	58.7 (t)	4.1–3.4 (m)	60.0 (t)
C_3	6.2–5.75 (m)	124.9	4.8–4.5 (m)	41.9 (d)
C_4	5.6–5.4 (m)	124.3	4.1–3.4 (m)	35.9 (t)

[a] Multiplicity (s, d, t, q) as determined from off-resonance decoupled spectra.

monium ion such as **4** is readily susceptible to intramolecular attack by an adjacent sulfur atom. Thus, careful analysis (preferably by ^{13}C NMR) of the halogenation products formed from allylic sulfides is warranted in order to confirm the formation of the "expected" products.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Chemical shifts are reported in parts per million(s) relative to internal tetramethylsilane.

Materials. Allyl methyl sulfide was obtained from Aldrich Chemical Co. and used without further purification. Bromine was procured from J.T. Baker and was distilled from P_2O_5 prior to use.

1,3-Dibromo-2-(methylthio)propane (3). To a solution of 1.00 g (11.3 mmol) of allyl methyl sulfide in 10 mL of CCl_4 cooled to −10 °C in an CCl_4/CO_2 bath was added dropwise a solution of 1.80 g (11.3 mmol) of Br_2 in 5 mL of CCl_4, keeping the temperature below −10 °C. A yellow precipitate formed, which dissolved on warming to room temperature, giving a colorless solution. The CCl_4 was removed in vacuo to give 2.80 g (100%) of **3** as a colorless liquid.

1,2-Dibromo-3-(methylthio)propane (2). A $CDCl_3$ (1 M) solution of **3** was heated at reflux for 5 h or **3** was heated without solvent for 1 h at 115 °C to give a mixture of **2** and **3** in an 82:18 ratio, as shown by ^{13}C NMR. Distillation via Kugelrohr at 98–102 °C (0.2 mmHg) gave a colorless liquid in 68% yield having a **2/3** ratio of 78:22.

Allyl Methyl Sulfone (7). An ice cold solution of 7.28 g (34.0 mmol) of $NaIO_4$ in 70 mL of H_2O containing 1.00 g (11.3 mmol) of allyl methyl sulfide stood at room temperature for 30 h and then at 5 °C for 2 days. The aqueous solution was decanted from the inorganic crystals and extracted with CH_2Cl_2 (4 × 15 mL). The combined organic phase was washed with 10 mL of H_2O and dried ($MgSO_4$), filtered, and concentrated in vacuo to give 0.77 g (56%) of a colorless liquid that was shown to be 93% sulfone and 7% sulfoxide by ^{13}C NMR.

2,3-Dibromo-1-propyl Methyl Sulfone (8). To a solution of 0.51 g (4.3 mmol) of **7** in 3 mL of $CDCl_3$, cooled to −60 °C, was added a solution of 0.68 g (4.3 mmol) of Br_2 in 2 mL of $CDCl_3$. After 10 min at room temperature, ^{13}C NMR showed 100% **8**, and concentration in vacuo gave 1.19 g (100%) of **8** as a light yellow liquid.

Anal. Calcd for $C_4H_8SO_2Br_2$: C, 17.16; H, 2.88; S, 11.45. Found: C, 17.37; H, 2.93; S, 11.34.

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Registry No. 1, 10152-76-8; 2, 86823-45-2; 3, 86823-46-3.

Cation Exchange Resin (Hydrogen Form) Assisted Decomposition of 1-Aryl-3,3-dialkyltriazenes. A Mild and Efficient Method for the Synthesis of Aryl Iodides

Nagichettiar Satyamurthy and Jorge R. Barrio*

Division of Biophysics, Departments of Radiological Sciences and Pharmacology, School of Medicine and Laboratory of Nuclear Medicine, Laboratories of Biomedical and Environmental Sciences, University of California, Los Angeles, Los Angeles, California 90024

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The wide use of aromatic radioiodinated compounds in medicinal diagnostic procedures[1] has warranted the development of a mild and efficient method for the regiospecific incorporation of iodine into an aromatic nucleus. Access to these compounds commonly involve electrophilic halogenations by the in situ generation of radiohalonium ions, which generally require highly activated aromatic rings[2] and result in the formation of a mixture of isomers.[3] Recent work involving the cleavage of aryl–silicon[4] or aryl–boron[5] bonds with electrophilic halonium ions has been directed toward developing more selective methods for this reaction.

On the other hand, nucleophilic substitutions by the Sandmeyer reaction, and its subsequent modifications,[6]

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