the resulting powder [110° (0.05 mm), 48 hr; C_6H_6OCs dried 130° (0.05 mm), 96 hr].

Phenoxide	Neut equiv Found	Neut equiv Theory
C_6H_5OK	132.2, 132.2	132.0
C_6H_5ONa	116.5, 116.2	116.0
p-$CH_3C_6H_4ONa$	146.8, 147.2	146.0
C_6H_5OCs	226	226.0

Polyglyme Preparation [$CH_3O(CH_2CH_2O)_{20}CH_3$].—Polyethylene glycol-1000 (a mixture of glycols of C_{18}–C_{24}; 500 g, 0.50 mol) was stirred with 54 g (1.0 mol) of CH_3ONa for 18 hr at 110°. Then low-boiling substances were removed under vacuum [110° (3 hr), 28.2 g liquid, 32 g theory]. To the dark brown, viscous solution CH_3I (206 g, 1.45 mol) was added gradually. The temperature rose to 155° quickly. Refluxing was for 1 hr, yielding a neutral, clear solution. On cooling the product was a clear solution. Of this residue, 310 g in 2000 ml of distilled water was slowly filtered through an Amberlite MB-1 column (450 mequiv, a strong mixed ion exchange resin). Ellution was carried out with 1500 ml of distilled water. The clear, neutral liquors (negative for I^- with $AgNO_3$) were carefully dried to 160° (0.02 mm) for 20 hr.

Anal. Found: C, 54.01; H, 9.11; O, 37.33; ash, 0.0; mol wt (vapor phase osmometer, 37°, THF), 1006 (c = 37.8 mg/g solvent); 934 (c = 14.0 mg/g solvent); nmr (neat, TMS) δ −3.51 (s, CH_2), 3.25 (s, OCH_3); 3.20 ± 0.8 wt % CH_3 (for mol wt 1000, 3.00 wt % CH_3 calcd).

The kinetic reactions were carried out in a dry 250-ml mechanically stirred flask (under N_2) which was immersed in an oil bath (160 ± 0.05°). The accurately weighed metal phenoxide and solvent were placed into the flask (drybox) and the equivalent amount of halophenyl sulfone was placed into a small sealed tube in the reaction flask. All was then thermally equilibrated. At time zero the glass tube was crushed and rapid stirring quickly (<30 sec) resulted in a homogeneous solution (no temperature change). Most kinetic runs were carried out with 1 mol of phenoxide/1 mol of halo sulfone, at 160.0° and at about 0.19 mol/l. concentration. The densities of the solvents were measured at 160°.

From time to time weighed samples were withdrawn (syringe) and titrated with 0.1 N HCl (pH meter) or added to glacial acetic acid for subsequent gas chromatography. An F & M 720 instrument using a 2 m × 0.25 in., 10% OV-1 on Chromosorb column was used.[30] Product studies showed that these reactions resulted in at least 96% product which was free of corresponding isomers.

The kinetic constants were evaluated by the differential method.[31]

The titrated base concentration ([OH] as moles of unreacted phenoxide per liter of solution) was first plotted against time t. Next the logarithms of the slopes $\ln d[OH]/dt$ of the smoothed decay curve, at various times t, were then plotted against $\ln [OH]$. This results in a straight line of slope n and an intercept (at $\ln [OH] = 0$) of $\ln k_2$.[32] The empirical reaction order n can be evaluated with a fair degree of accuracy by this method. A plot of $[OH]^{1-k}$ against t (slope k_2) yields a more accurate method for determining the reaction rate constant.

When potassium phenoxide was used in sufficient excess (0.241 mol C_6H_5OH/l. solution) then a first-order plot was obtained (for p-$ClC_6H_4SO_2C_6H_5$ disappearance). The reaction rate constant for p-$FC_6H_4SO_2C_6H_5$ was determined by a competitive experiment with p-$ClC_6H_4SO_2C_6H_5$ using deficient potassium phenoxide (initial concentration of p-$FC_6H_4SO_2C_6H_5$, 0.30 mol/l., C_6H_5OK, 0.24 mol/l., p-$ClC_6H_4SO_2C_6H_5$, 0.0554 mol/l.).[33]

Registry No.—Diglyme, 11-96-6; triglyme, 112-49-2; tetraglyme, 143-24-8; polyglyme, 24991-55-7.

Acknowledgments.—Mr. John Puckhaber carried out a large part of this experimental study. The analyses were performed by the European Research Laboratories, Brussels, Belgium. Miss A. Hammerich carried out the nmr work.

[30] The rate constant calculated from the caustic titration data was the same as that from $ClC_6H_4SO_2C_6H_5$ disappearance, p-$C_6H_5OC_6H_4SO_2$-C_6H_5 appearance (gas chromatography), or chloride ion appearance (Ag^+ titration). Ten to twelve samples per run were taken (~ 80% conversion).

[31] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 82.

[32] $d[OH]/dt = k_2[OH]^k$; therefore $\ln d[OH]/dt = \ln k_2 + n \ln [OH]$.

[33] The underlying assumption here is that the reaction order for the chlorophenyl sulfone is the same as that for the fluorophenyl sulfone.

The Reaction of Halothianaphthenes with Metal Amides[1]

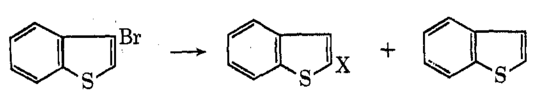
MANFRED G. REINECKE* AND T. A. HOLLINGWORTH

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Received July 21, 1972

The 2-halothianaphthenes react with metal amides in liquid ammonia to give the 3 isomers, which are stable under the reaction conditions. No amines or polyhalo compounds were detected. 2,3-Dibromothianaphthene is converted to 3-bromothianaphthene either with or without added thianaphthene. The former instance suggests an intermolecular transhalogenation involving carbanions and the latter a dehalogenation *via* $BrNH_2$.

The reaction of haloaromatic compounds with metal amides in liquid ammonia as a potential route to aryne intermediates[2] has been investigated in our laboratories for a variety of thiophenes.[3-6] Although arynes are apparently not implicated in these reactions,[3,4] the related thianaphthene system is reported to react with potassium hydroxide[7] or piperidine[8] to give both dehalogenation and cine substitution[9] (eq 1), the latter process suggesting[11,12] the possible intermediacy of 2,3-dehydrothianaphthene. Since similar processes observed with thiophenes[3-6] and metal



(1)

1 2a, X = OH b, X = NC_5H_{10} 3

[1] Taken from the Master's Thesis of T. A. H., Texas Christian University, 1967.

[2] J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Amer. Chem. Soc.*, **78**, 601 (1956).

[3] M. G. Reinecke and H. W. Adickes, *ibid.*, **90**, 511 (1968).

[4] M. G. Reinecke, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), C68 (1969).

[5] M. G. Reinecke, H. W. Adickes, and C. Pyun, *J. Org. Chem.*, **36**, 2690 (1971).

[6] M. G. Reinecke, H. W. Adickes, and C. Pyun, *ibid.*, **36**, 3820 (1971).

[7] G. Komppa and S. Weckman, *J. Prakt. Chem.*, **138**, 109 (1933).

[8] K. R. Brower and E. D. Amstutz, *J. Org. Chem.*, **19**, 411 (1954).

[9] The reaction of 3-bromothianaphthene and piperidine reported in ref 8 has now been reinvestigated in this laboratory[10] and found to undergo primarily normal and not cine substitution.

[10] W. B. Mohr, Master's Thesis, T. C. U., 1969; manuscript in preparation.

[11] H. J. den Hertog and H. C. van der Plas, *Advan. Heterocycl. Chem.*, **4**, 121 (1965).

[12] T. Kauffmann, *Angew. Chem., Int. Ed. Engl.*, **4**, 543 (1965).

TABLE I

REACTIONS OF HALOTHIANAPHTHENES WITH METAL AMIDES

Reactants	Amide	Time	Products (yield, %)
3-Bromothianaphthene (**1**)	KNH_2	3 hr	**1** (72)
3-Bromothianaphthene (**1**)	$NaNH_2$	3 hr	**1** (65)
2-Bromothianaphthene (**4**)	KNH_2	15 min	**1** (49)
2-Bromothianaphthene (**4**)	$NaNH_2$	15 min	**1** (45)
2-Bromothianaphthene (**4**)	$NaNH_2$	2 min	**1** (39), **4** (23)
3-Iodothianaphthene (**7**)	KNH_2	3 hr	**7** (43)
3-Iodothianaphthene (**7**)	$NaNH_2$	3 hr	**7** (52)
2-Iodothianaphthene (**8**)	KNH_2	15 min	*a*
2-Iodothianaphthene (**8**)	$NaNH_2$	15 min	**7** (4)
2,3-Dibromothianaphthene (**5**)[b]	KNH_2	15 min	**1** (68), **3** (4)
2-Aminothianaphthene (**9**) (5 mmol) + **4** (5 mmol)	$NaNH_2$	15 min	**1** (47), **9**[c] (10)
5 (10.0 mmol) + **3** (11.0 mmol)	$NaNH_2$	15 min	**5** (0.3 mmol), **1** (14.1 mmol), **3** (1.8 mmol)
5 (9.4 mmol) + **3** (9.5 mmol)	$NaNH_2$	2 min	**5** (1.6 mmol), **4** (0.8 mmol), **3** (1.8 mmol), **1** (9.8 mmol)

[a] No identifiable product. [b] <1% **1** as impurity. [c] Isolated as the acetamide, mp 218–222° (lit.[14] mp 222–226°), and identified by comparison of its ir spectra with that of an authentic sample.

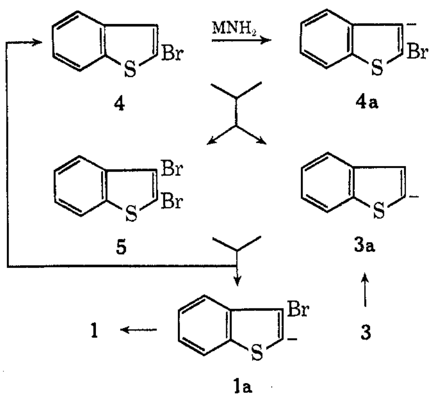
amides proceed *via* a transhalogenation mechanism,[3,4] it was of interest to investigate the nature and mechanism of the reactions of halothianaphthenes with metal amides in liquid ammonia.

In contrast to the previous observations (eq 1), however, 3-bromothianaphthene (**1**) is recovered in 75 and 72% yield when treated with 6 equiv of $NaNH_2$ or KNH_2, respectively, for 3 hr. No traces of either 2- or 3-aminothianaphthene could be detected, although they might have been formed and then decomposed[13,14] during the course of the reaction as indicated by the presence of tars. Under the same conditions 2-bromothianaphthene (**3**) is completely reacted in 15 min to give the 3 isomer **1** in 45 and 49% yield.[15] Once again no amines could be detected, even at reduced reaction times and in spite of the fact that added 2-aminothianaphthene was easily detected (10% recovery) in the reaction mixture. These results are paralleled with the 2- and 3-iodothianaphthenes, although lower yields and more tars are obtained (Table I).

The behavior of the halothianaphthenes toward metal amides is similar to that of the halothiophenes[3] in that the 2 isomers are more reactive than the 3 isomers and in that the former rearrange to the latter. The behavior diverges in that no amino compounds were detected from the thianaphthene systems and no dependence of product composition on concentration[4,16] or nature of the metal amide[4] was observed. Furthermore, it was not possible to detect any polybromothianaphthenes in the reaction mixtures, as would have been expected for a transhalogenation mechanism.[3,4]

Since the absence of polybromo compounds such as 2,3-dibromothianaphthene (**5**) may simply be due to their low concentration and/or high reactivity in the reaction media, a further test of the feasibility of this mechanism was desirable. Consequently, an equimolar mixture of the possible intermediates[3,4] **3** and **5** was subjected to the reaction conditions and 3-bromothianaphthene (**1**) was isolated in 67% yield (based on available thianaphthene rings). At reduced reaction times it was also possible to detect the presence of 2-bromothianaphthene (**4**). Both these results are consistent with an intermolecular transhalogenation mechanism (Scheme I) involving nucleophilic displacements by carbanions on halogen and leading eventually to the most stable carbanion **1a**. Analogies for this mechanism are found in the benzene,[17] thiophene,[3,4,18] isothiazole,[19] and imidazole[20] systems, and in the fact that 2,3-dibromothiophene (**5**) undergoes selective halogen–metal interchange at the 2 position with butyllithium.[21]

SCHEME I



That another process besides this may be operative, however, is shown by the observation that **5** is debrominated to **1** in 68% yield in the *absence* of any thianaphthene (**3**). Except for a trace of thianaphthene (**3**) as *product* no other compounds could be detected.

In order to explain this result, some nucleophile (Nu) other than the two carbanions **3a** and **4a** in Scheme I

---

[13] P. Friedländer and A. Laske, *Justus Liebigs Ann. Chem.*, **351**, 412 (1907).

[14] G. W. Stacy, F. W. Villaescusa, and T. E. Wollner, *J. Org. Chem.*, **30**, 4074 (1965).

[15] On subsequent larger scale runs yields as high as 87% have been obtained.[6]

[16] H. W. Adickes, Ph.D. Dissertation, Texas Christian University, 1968.

[17] J. F. Bunnett, *Accounts Chem. Res.*, **5**, 139 (1972).

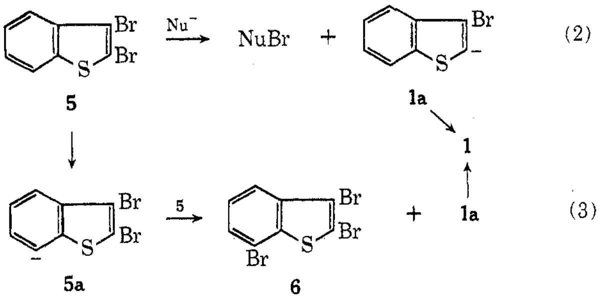
[18] S. Gronowitz, *Advan. Heterocycl. Chem.*, **1**, 75 (1963).

[19] D. A. de Bie and H. C. van der Plas, *Tetrahedron Lett.*, 3905 (1968).

[20] D. A. de Bie and H. C. van der Plas, *Recl. Trav. Chim. Pays-Bas*, **88**, 1246 (1969).

[21] W. Reid and H. Bender, *Chem. Ber.*, **88**, 34 (1955).

must be able to carry out the displacement on bromine (eq 2). By analogy with the known reactivity of dibenzothiophene toward strong bases,[22] one such possibility might be the 7 carbanion **5a**. Disproportionation (eq 3) would lead to the observed product, **1**, and the tribromo compound **6**, which could then undergo the base-catalyzed halogen dance[17] to give still other polybromo compounds and/or amination to give unstable bromo amines.



(2)

(3)

Another possibility is that the nucleophile in eq 2 is solvent derived (*i.e.*, NH_2^-), as in the case of the DMSO/alkoxide catalyzed debromination of related aryl bromides.[17,23] The expected product in this instance, $BrNH_2$, would react further with amide ion to give hydrazine (eq 4) which would have been undetected by the work-up procedure. In support of this suggestion 1,1′-bipiperidine can be isolated from the reactions of halothiophenes with metal piperidides and piperidine.[24]

$$NH_2Br + NH_2^- \longrightarrow H_2NNH_2 + Br^- \qquad (4)$$

The conclusion to be drawn from these results is that the rearrangement of halothianaphthenes with metal amides in liquid ammonia is a further example of the previously observed transhalogenation mechanisms[3,4,17–20] with the added feature that amide ions as well as carbanions may act to remove positive halogen atoms.[25]

Experimental Section

Melting points are uncorrected. Infrared spectra of liquids were taken as films on a Beckman IR-10 and solids as KBr discs on a Perkin-Elmer 237 spectrophotometer. Gas chromatographic analyses were carried out on an Aerograph Model A-700 instrument with a 30 ft × 0.25 in. column packed with 10% Carbowax 4000 on Gas-Chrom R.

Starting Materials.—3-Bromothianaphthene (**1**),[27] 2-bromothianaphthene (**4**),[28] 2- and 3-iodothianaphthene,[29] 2,3-dibromothianaphthene (**5**),[21] and 2-aminothianaphthene[14] were prepared by the cited literature procedures and their purity was checked by glc. The monohalothianaphthenes were furthermore purified by glc prior to use.

General Procedure for the Reaction of Halothianaphthenes with Metal Amides.—To a fresh preparation of 0.06 mol of metal amide[30] in 500 ml of liquid NH_3 in a 2-l. Morton flask equipped with a stirrer and a Dry Ice–acetone condenser was rapidly added 0.01 mol of the appropriate halothianaphthene or mixture of thianaphthenes (Table I). After the reaction had proceeded for the desired length of time at −33°, 0.065 mol of NH_4Cl was added, the NH_3 was evaporated under a stream of dry N_2, and a mixture of 100 ml of ether and 200 ml of H_2O was added. The separated water layer was extracted with three 100-ml portions of ether and the combined ether extracts were washed with four 50-ml portions of 1 *N* HCl. The combined acid washes were basified with 50% NaOH and extracted with four 50-ml portions of ether, and 40 ml of Ac_2O was added to the combined ether layers. After 12 hr at room temperature the mixture was taken to dryness on a rotary evaporator and the residue was examined for acetamidothianaphthenes.

The original ether extracts were dried ($CaCl_2$) and fractionally distilled. The products in the distillate were identified by comparing their ir spectra after collection from the glc with those of authentic samples. Quantitative analysis was based on the relative areas of each component in the glc trace taking into account the molar response factor for each compound.

The results of these reactions are summarized in Table I.

Registry No.—**1**, 7342-82-7; **3**, 95-15-8; **4**, 5394-13-8; **5**, 6287-82-7; **7**, 36748-88-6; **8**, 36748-89-7; **9**, 4521-30-6; KNH_2, 17242-52-3; $NaNH_2$, 7782-92-5.

Acknowledgment.—This research was supported by the Robert A. Welch Foundation and the TCU Research Foundation.

---

(22) H. Gilman and R. L. Bebb, *J. Amer. Chem. Soc.*, **61**, 109 (1939).

(23) J. F. Bunnett and R. R. Victor, *ibid.*, **90**, 810 (1968); J. M. Barker, I. G. C. Coutts, and P. R. Huddleston, *Chem. Commun.*, 615 (1972).

(24) C. Pyun, unpublished results.

(25) A recent independent study[26] on thianaphthene and related heterocycles has led to an identical conclusion and also considered the possible role of $BrNH_2$ as a bromine-transfer agent in these systems.

(26) D. A. de Bie, H. C. van der Plas, G. Geurtsen, and K. Nijdam, *Recl. Trav. Chim. Pays-Bas*, submitted for publication; we thank Professor van der Plas for making this manuscript available to us prior to publication.

(27) J. Szmuszkovicz and E. Modest, *J. Amer. Chem. Soc.*, **72**, 571 (1950).

(28) D. A. Shirley and M. D. Cameron, *ibid.*, **74**, 664 (1952).

(29) R. Gaertner, *ibid.*, **74**, 4950 (1952).

(30) K. W. Greenlee and A. L. Henne, *Inorg. Syn.*, **2**, 128 (1946).