

(CH₃)₂COH grouping of 21). The remainder of the spectrum was consistent with these assignments, showing multiplets at 5.5, 5.04, 4.8, and 4.5 (vinyl H) and 1.65 ppm (vinyl CH₃) with appropriate areas.

Registry No.—*cis*-1, 36807-98-4; *trans*-1, 36807-99-5; 13, 36808-00-1; 15, 36808-01-2; 19, 36803-64-2; 20, 36803-65-3; 2,3,5-trimethyl-2,4-hexadiene, 1726-48-3.

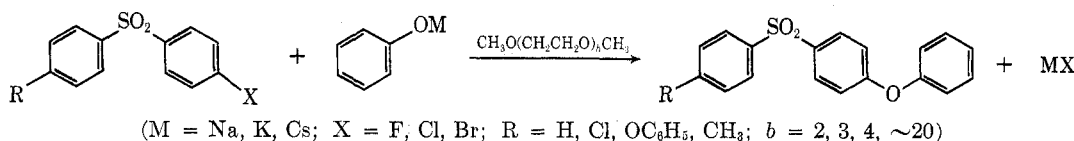
The Reaction of Haloaryl Sulfones with Alkali Phenoxides. The Effects of Polyglyme Solvents and Other Variables

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The reaction of alkali phenoxides with *p*-halophenyl (para-substituted phenyl) sulfones



has been studied in the aprotic dimethyl ether of polyethylene glycol solvents at 160°. This nucleophilic aromatic displacement reaction is first order in halo sulfone and of fractional (~0.5) order in phenoxide ion. The active nucleophile is the monomeric anion which results from a dissociation of the alkali phenoxide aggregate. The ether solvent chain length has a strong influence on the reaction rate: when $b \cong 20$ the reaction is about 25 times faster than when $b = 2$. The reaction rate increases in the order Cl < Br < F, Na << K < Cs; (R) CH₃ < H ~ OC₆H₅ < Cl. When dimethyl sulfoxide is used as solvent in place of these polyethers, a reaction rate enhancement of about 10³ is found ($b = 2$, X = Cl, M = K, R = H).

The rates of nucleophilic aromatic displacement reactions¹⁻³ are strongly accelerated by the nature and number of electron-withdrawing groups attached to the aromatic ring undergoing substitution, by both the nature of the attacking nucleophile and leaving group, by the solvent and cation type, and frequently by the presence of "copper."⁴ The combination of dipolar, aprotic solvent,⁵ strong electron-withdrawing groups (NO₂, CN, SO₂), a very nucleophilic anion, and a readily polarizable cation (K, Rb, Cs) appears to maximize the rate of halide (F ≫ Cl > Br ~ I) displacement from aromatic rings.²

There is evidence that the rates of aliphatic displacement reactions are influenced by the nature and chain length of polyethylene glycol ether-type solvents. Thus, the rate of reaction of potassium or sodium phenoxide with *n*-butyl bromide in dimethyl ether of polyethylene glycol [CH₃O(CH₂CH₂O)_bCH₃] increases considerably with increase in b .^{6,7} When potassium phenoxide is used and $b = 6$, then the reaction is about 200 times faster than when $b = 1$ (also $b = 2$, rate = 8; $b = 3$, rate = 51; $b = 4$, rate = 72). Similar evidence exists for the isomerization of 3-butenylbenzene to 1-butenylbenzene with potassium *tert*-butoxide in these solvents.⁸

One purpose of this investigation was to see whether this effect is also observed in nucleophilic aromatic displacement reactions, in particular on haloaromatic sulfones. A number of other features, *e.g.*, reaction

order, impurity effects, solvent and leaving group nature, etc., were also examined.

Results and Discussion

A. Reaction Order and Mechanism.—The reaction of *p*-ClC₆H₄SO₂C₆H₅ with potassium phenoxide in diglyme⁹ at 160.0°, 1.0 mol phenoxide/1 mol halo sulfone and at about 0.19 mol/l. reagent concentrations, follows a fractional order rate law ($k_2 = 0.021 \pm 0.001$ l./mol min; overall $n = 1.41$). The order, relative to the haloaromatic sulfone, is 1.0, since the use of a large excess of base (10:1) results in a pseudo-first-order reaction.¹⁰ A variation of the reagent concentrations by a factor of one-half (at 1.0 mol phenoxide/1 mol sulfone) results in no appreciable change in the second-order rate constant (0.019 l./mol min) nor in a deviation from the fractional order nature of the reaction ($n = 1.41$).

Similar displacement reactions involving charged nucleophiles in aprotic media are frequently of fractional order^{6-8,11,12} owing to aggregation of the nucleophile to polymers and because only the monomer appears as the reactive species.¹¹ Thus, in the reaction of *n*-butyl bromide with alkali phenoxide in glyme solvents, it was found⁶ that the reaction order with respect to the phenoxide was "far from unity" and almost zero when sodium phenoxide was used. There also appeared to be an increase in the phenoxide order with

(1) F. Pietra, *Quart. Rev., Chem. Soc.*, **23**, 504 (1969).

(2) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, New York, N. Y., 1968.

(3) J. Sauer and R. Huisgen, *Angew. Chem.*, **72**, 294 (1960).

(4) R. G. R. Bacon and H. A. O. Hill, *Quart. Rev., Chem. Soc.*, **19**, 95 (1965).

(5) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(6) J. Ugelstad, A. Berge, and H. Liston, *Acta Chem. Scand.*, **19**, 208 (1965).

(7) A. Berge and J. Ugelstad, *ibid.*, **19**, 742 (1965).

(8) J. Ugelstad and O. A. Rokstad, *ibid.*, **18**, 474 (1964).

(9) CH₃O(CH₂CH₂O)_bCH₃; $b = 2$, diglyme; $b = 3$, triglyme; etc.

(10) Up to at least 85% conversion; the calculated second-order rate constant was 0.042 l./mol min. This is about twice the "normal" k_2 (at 1.0 mol phenoxide/1 mol halo sulfone) of 0.021 l./mol min; the difference may be due to a salt effect. When potassium phenoxide was treated with excess (10:1) *p*-ClC₆H₄SO₂C₆H₅ then $k_2 = 0.021$ l./mol min and $n = 0.66$. The reason for the deviation from the expected $n = 0.4$ is not known (duplicate experiments).

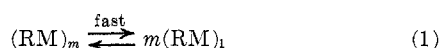
(11) R. A. H. Casling, A. G. Evans, and N. H. Rees, *J. Chem. Soc. B*, 519 (1966).

(12) H. Weingarten, *J. Org. Chem.*, **29**, 977, 3624 (1964).

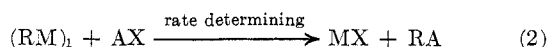
increase in glyme chain length.¹³ Similarly, the reaction of potassium phenoxide with bromobenzene (Ullmann condensation) in diglyme showed that the reaction order with respect to the phenoxide was between two and one.¹² Other investigators¹¹ showed that in the reaction of *tert*-butyllithium with fluorene or diphenylethane, the reaction order with respect to the lithium compound was 0.25. This was ascribed to the tetrameric state of *tert*-butyllithium in benzene (when *n*-butyllithium was used the order was 0.18, *e.g.*, a hexameric polymer).

In all of these cases, as well as the reactions investigated here, a rapid monomer-polymer equilibrium must precede the rate-determining step of the reaction.¹⁴

The actual (RM)₁ (reactive monomer concentration) is therefore dependent upon the equilibrium (eq 1).



The subsequent step (eq 2) is the displacement of the aromatic halide. The rate order $F \gg Cl \sim Br$ (*vide*



infra, Table III) suggests that the phenoxide bond formation is the critical step.³ No colored intermediates¹⁵ suggestive of Meisenheimer-type transients were observed.

B. Effect of Solvent Chain Length and Type.—When the chain length of the dimethyl ether of polyethylene glycol is increased a corresponding increase in the reaction rate is observed (Table I). Polyglyme ($b \cong 20$) results in a 25-fold increase in the rate over the rate in diglyme; simultaneously there is a considerable increase in the order of the reaction with respect to the potassium phenoxide. With diglyme the total order is 1.41; with polyglyme this rises to 1.93. This would indicate that the polyglyme causes a shift in the phenoxide monomer-polymer equilibrium to the monomer side.¹⁷ It is unlikely that this glyme series differs appreciably in their dielectric constants,⁷ hence a rate enhancement due to a dielectric effect is ruled out. It is most likely that particularly the polyglyme is a far better cation solvating solvent than is diglyme.²⁰ This is reminiscent of Pedersen's crown ethers,²¹ which form stable complexes principally with group I cations.

(13) These authors^{6,7} did not consider that these phenoxides could be polymers in solution. Their measurements were correlated *via* the initial reaction rates and the approximately first-order rate constants (1 mol phenoxide per 1 mol RBr). If conversions are low (~10%) then this treatment is semiquantitatively acceptable.

(14) Potassium phenoxide used here is approximately a trimer in THF (degrees of polymerization = 3.2; 37°, ~1 wt % concentration, osmometry). The molecular weight decreases to about 200 in boiling diglyme (degree of polymerization = 1.5; 160°, 2.5 wt % concentration, ebullioscopically).

(15) During the reaction of *p,p'*-dichlorodiphenyl sulfone with the disodium salt of 2,2-bis(4-hydroxyphenyl)propane in DMSO at 150°, a transient, vivid orange-yellow color is observed which is discharged on termination of the reaction.¹⁶

(16) R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale, and C. N. Merriam, *J. Polym. Sci., Part A-1*, **5**, 2375 (1967).

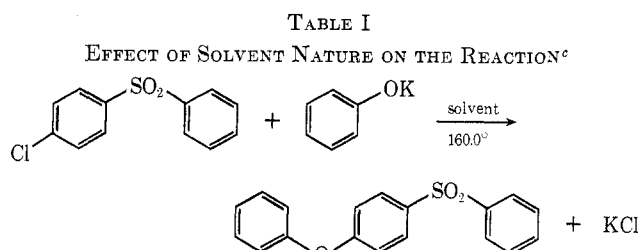
(17) Unfortunately, it is not possible to measure the potassium phenoxide molecular weight directly in polyglyme. Ultraviolet or nuclear magnetic resonance techniques might confirm this equilibrium shift.^{18,19}

(18) J. Smid, *Angew. Chem.*, **84**, 127 (1972).

(19) J. F. Garst, R. A. Klein, D. Walmsley, and E. R. Zabolotny, *J. Amer. Chem. Soc.*, **87**, 4080 (1965).

(20) In the preparation of polyglyme it was observed that at 25° NaI forms stable solutions at the 23 wt % level (2 mol of NaI/1 mol of polyglyme)

(21) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, **84**, 16 (1972), and previous publications.

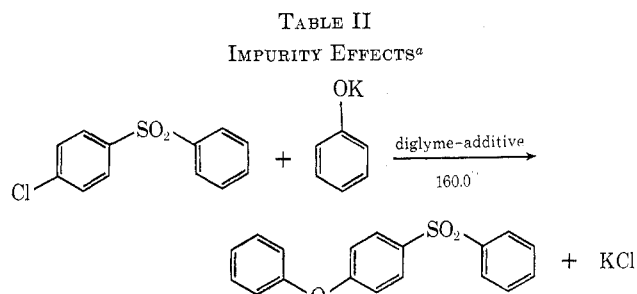


Solvent	Relative rate	k_2 , l./mol min	n^a
CH ₃ O(CH ₂ CH ₂ O) ₂ CH ₃ (diglyme)	1.0	0.021 ± 0.001	1.41
CH ₃ O(CH ₂ CH ₂ O) ₃ CH ₃ (triglyme)	4.3	0.090 ± 0.01	1.65
CH ₃ O(CH ₂ CH ₂ O) ₄ CH ₃ (tetraglyme)	8.8	0.184 ± 0.03	1.68
CH ₃ O(CH ₂ CH ₂ O) ₂₀ CH ₃ (polyglyme)	24.8	0.522	1.93
99 wt % diglyme + 1 wt % DMSO ^b	1.4	0.030	1.41
90 wt % diglyme + 10 wt % DMSO	7.6	0.160	1.38
75 wt % diglyme + 25 wt % DMSO	75	1.57	1.58

^a Total reaction order. ^b Dimethyl sulfoxide. ^c 1 mol of phenoxide/1 mol of halo sulfone; 0.19 mol/l. concentration.

The addition of DMSO to diglyme causes similar reaction rate enhancement. At a 25 wt % level (about 5 mol DMSO/1 mol potassium phenoxide) the reaction is 75 times as fast as in pure diglyme and three times as fast as in polyglyme. The reaction order does not appear to increase; at 25 wt % DMSO, n is only 1.58, far below the 1.93 for pure polyglyme.²²

C. Impurity Effects.—Table II shows the rate

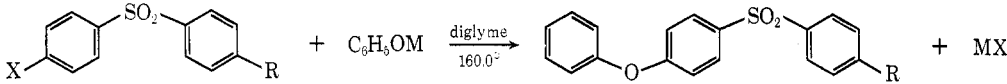


Impurity	Concn. mol/mol phenoxide	k_2 , l./mol min	Relative rate
None		0.021 ± 0.001	1.00
Ethylene carbonate	0.245	0.026	1.2
[C ₆ H ₅ NCH ₂ CH ₂] ₄ ^b	0.045	0.019	0.9
DMSO	1.1	0.030	1.4
Crown-18 ^c	0.12	0.031	1.5
CuBr	0.03	0.028	1.3
CuOAc	0.0355	0.021	1.0
Cu(acac) ₂	0.164	0.024	1.1

^a The overall reaction orders were 1.4 ± 0.1; 1 mol phenoxide/1 mol halo sulfone; 0.19 mol/l. ^b Models show that the "hole" in this cyclic compound is too small to accommodate a potassium ion. ^c Dibenzo[18]-crown-6.²¹

(22) In pure DMSO the reaction rate is estimated to be 10³ times faster than in diglyme (160°). This is in good agreement with others²³ who found the reaction rate of potassium phenoxide with the first chlorine of *p,p'*-dichlorodiphenyl sulfone to be about 750 times as fast in DMSO (160°, extrapolated) as *p*-chlorophenyl(phenyl) sulfone and potassium phenoxide react in diglyme (160°).

(23) S. R. Schulz and A. L. Baron, *Advan. Chem. Ser.*, **91**, 692 (1969).

TABLE III
 EFFECT OF PHENOXIDE CATION, SULFONE SUBSTITUENTS AND SULFONE HALOGEN^c


Registry no.	X	R	M	k_2 , l./mol min	n	Relative rate
80-00-2	Cl	H	K ^d	0.021 ± 0.001	1.41	(1.00)
312-31-2	F ^a	H	K	1.44		68.7
23038-36-0	Br	H	K	0.068	1.58	3.2
	Cl	H	Na ^a	0.000336	1.08	0.016
	Cl	H	Cs ^f	0.122	1.53	5.8
5184-71-4	Cl	CH ₃	K	0.0155	1.42	0.75
80-07-9	Cl ^b	Cl	K	0.054 ^b		2.5
36794-63-5	Cl	OC ₆ H ₅	K	0.0235	1.50	1.1

^a Run competitively against *p*-ClC₆H₄SO₂C₆H₅ with deficient caustic. ^b First chlorine displaced. ^c 1 mol phenoxide/1 mol halo sulfone; 0.19 mol/l. ^d Registry no., 100-67-4. ^e Registry no., 139-02-6. ^f Registry no., 1120-91-8.

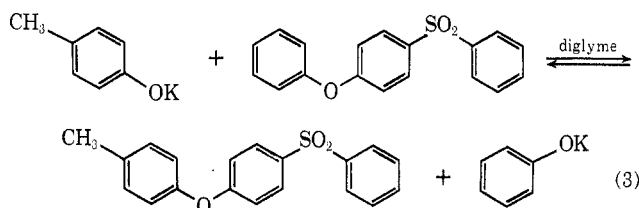
changes which took place when relatively small quantities of impurities were added to the displacement reaction. Weingarten¹² found that small quantities of impurities such as ethylene carbonate, in diglyme, greatly accelerated the reaction of bromobenzene with potassium phenoxide. Here this additive seemed to yield no substantial rate acceleration. Neither did small quantities of a cyclic amine, the crown-18 ether,^{21,24} nor DMSO. The addition of Cu⁺ or Cu²⁺ compounds, which acted as catalysts for the Ullmann condensation,¹² caused no appreciable rate change here.

D. Cation, Halogen, and Sulfone Substituent Effects.—Table III summarizes the results which were obtained when the nature of the sulfone halide (leaving group), the phenoxide cation, and the sulfone substituent were varied. As expected,^{3,16} the fluoride is considerably more reactive than the chloride (69:1); the bromide is three times as fast as the chloride. The cation effect in this system is remarkable: Cs > K ≫ Na; this is in line with observations in similar systems.^{12,16} It is most probable that the highly polarizable potassium and cesium ions interact more effectively with diglyme than does the sodium cation. The total reaction orders n are in the expected direction—1.08 for sodium and 1.4–1.5 for the potassium and cesium ions, respectively. Sodium phenoxide, in this system, must have a fairly high degree of polymerization (~12) and little tendency to be depolymerized and solvated by diglyme.²⁶

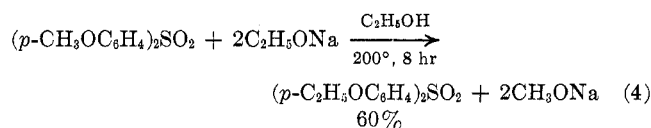
Substitution para in the other phenyl ring has only a marginal effect on the reaction rate. This is probably due to the inability of the sulfone group to transmit charge by induction or particularly resonance. Others²³ have also observed that the rate difference between the two chlorines in *p,p'*-chlorodiphenyl sulfone is small (about two); the first chlorine being displaced more readily than the second.

E. Further Reactions.—The reaction of alkali phenoxide with haloaromatic sulfones is essentially

quantitative. The products undergo further reaction (eq 3). This represents a cleavage of the C–O bond by



the nucleophile phenoxide. Relative to the chlorine displacement by phenoxide, this reaction is very slow ($k_2 = 8 \times 10^{-5}$ l./mol min in the direction to the right) and the equilibrium constant is 5.5.²⁷ Similar reactions^{28,29} (eq 4) take place in protic media (the respective alcohols) at high temperatures.



Experimental Section

The solvents diglyme, triglyme, and tetraglyme were purchased from the Aldrich Chemical Co. and fractionally distilled from over a generous quantity of LiAlH₄ after 24-hr reflux [diglyme bp 163–164°, triglyme bp 213–214°, tetraglyme bp 165° (14 mm)]. They were stored under N₂. The halo sulfones were purchased or prepared (*p*-XArSO₂Cl + Ar'H + 4% FeCl₃) and crystallized to a constant melting point.

Compd	Mp, °C
<i>p</i> -FC ₆ H ₄ SO ₂ C ₆ H ₅	111.5–112.5
<i>p</i> -ClC ₆ H ₄ SO ₂ C ₆ H ₅	92.5–93.5
<i>p</i> -BrC ₆ H ₄ SO ₂ C ₆ H ₅	108–109
<i>p</i> -ClC ₆ H ₄ SO ₂ C ₆ H ₄ CH ₃ - <i>p</i>	123–124
<i>p</i> -ClC ₆ H ₄ SO ₂ C ₆ H ₄ Cl- <i>p</i>	147–148
<i>p</i> -ClC ₆ H ₄ SO ₂ C ₆ H ₄ OC ₆ H ₅ - <i>p</i>	110–112

The metal phenoxides were prepared by mixing an ethanol solution of the phenol with 98% of the theoretical amount of metal hydroxide followed by rigorous and long-term drying of

(27) No reaction was observed between diphenyl sulfone and potassium phenoxide in diglyme at 160° in 3 days; the sulfone linkage is therefore immune to cleavage under the above reaction conditions.

(28) D. C. Allport, *Chem. Ind. (London)*, 606 (1965).

(29) G. W. Dalman and F. W. Neumann, *J. Amer. Chem. Soc.*, **90**, 1601 (1968).

(24) Various investigators found that the addition of these crown ethers to reactions involving charged nucleophiles results in appreciable rate enhancement; for example, the reaction of potassium phenoxide (0.025 *M*) with butyl bromide in dioxane is accelerated by a factor of 10⁴ when 0.05 *M* of such a cyclic ether is added.²⁶

(25) L. M. Thomassen, T. Ellingsen, and J. Ugelstad, *Acta Chem. Scand.*, **25**, 3024 (1971).

(26) In DMSO the cation effects are apparently not as pronounced,^{16,23} since *p,p'*-dichlorodiphenyl sulfone reacts at high rates with the disodium salts of various biphenols.

the resulting powder [110° (0.05 mm), 48 hr; C₆H₅OCs dried 130° (0.05 mm), 96 hr].

Phenoxide	Neut equiv	
	Found	Theory
C ₆ H ₅ OK	132.2, 132.2	132.0
C ₆ H ₅ ONa	116.5, 116.2	116.0
<i>p</i> -CH ₃ C ₆ H ₄ ONa	146.8, 147.2	146.0
C ₆ H ₅ OCs	226	226.0

Polyglyme Preparation [CH₂O(CH₂CH₂O)₂₀CH₃].—Polyethylene glycol-1000 (a mixture of glycols of C₁₈–C₂₄; 500 g, 0.50 mol) was stirred with 54 g (1.0 mol) of CH₃ONa 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 CH₃I (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). Elution was carried out with 1500 ml of distilled water. The clear, neutral liquors (negative for I⁻ with AgNO₃) 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, CH₂), 3.25 (s, OCH₃); 3.20 ± 0.8 wt % CH₃ (for mol wt 1000, 3.00 wt % CH₃ calcd).

The kinetic reactions were carried out in a dry 250-ml mechanically stirred flask (under N₂) 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 haloaryl 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 in 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-*n*} 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 C₆H₅OH/l. solution) then a first-order plot was obtained (for *p*-ClC₆H₄SO₂C₆H₅ disappearance). The reaction rate constant for *p*-FC₆H₄SO₂C₆H₅ was determined by a competitive experiment with *p*-ClC₆H₄SO₂C₆H₅ using deficient potassium phenoxide (initial concentration of *p*-FC₆H₄SO₂C₆H₅, 0.30 mol/l., C₆H₅OK, 0.24 mol/l., *p*-ClC₆H₄SO₂C₆H₅, 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 ClC₆H₄SO₂C₆H₅ disappearance, *p*-C₆H₅OC₆H₄SO₂-C₆H₅ 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) $d[\text{OH}]/dt = k_2[\text{OH}]^n$; therefore $\ln d[\text{OH}]/dt = \ln k_2 + n \ln [\text{OH}]$.

(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 Amides¹

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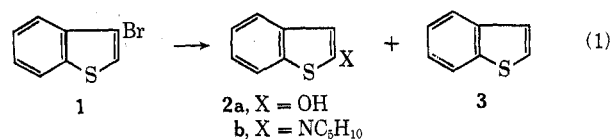
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The 2-halothianaphthenes react with metal amides in liquid ammonia to give the 3 isomers, which are stable under the reaction conditions. No amines or polyhalo compounds were detected. 2,3-Dibromothianaphthene is converted to 3-bromothianaphthene either with or without added thianaphthene. The former instance suggests an intermolecular transhalogenation involving carbanions and the latter a dehalogenation *via* BrNH₂.

The reaction of haloaromatic compounds with metal amides in liquid ammonia as a potential route to aryne intermediates² 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 hydroxide⁷ or piperidine⁸ to

give both dehalogenation and cine substitution⁹ (eq 1), the latter process suggesting^{11,12} the possible inter-



mediacy of 2,3-dehydrothianaphthene. Since similar processes observed with thiophenes³⁻⁶ and metal

(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 laboratory¹⁰ 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).