had peaks at δ 7.48 (m, 7) and 2.50 (s, 3), and was almost identical with that of compound XV except for the 1-proton multiplet at δ 8.29 assigned to the number eight hydrogen.[8] Not enough of this compound could be isolated for a carbon-hydrogen analysis.

The acidic fraction products (XI-XIV) were analyzed as described[5] for all runs except 6-9 where a 5 ft by $^1/_8$ in. column packed with a mixture of 1% SE-30 and 1% Carbowax 20M on 80-100 mesh Varaport 30 using a program from 150 to 167° at a rate of 0.5° per min was used. Results are listed in Table I. The retention times for compounds XI-XIV were compared with those displayed by authentic samples of those compounds as well as with those shown by the same products obtained in the 1-bromonaphthalene reaction (runs 1 and 2, Table I).

Registry No.—1-Bromonaphthalene, 90-11-9; 2-bromonaphthalene, 580-13-2; 1-iodonaphthalene, 90-14-2; 2-iodonaphthalene, 612-55-5; 1-chloronaphthalene, 90-13-1; 2-chloronaphthalene, 91-58-7; 1-fluoronaphthalene, 321-38-0; 2-fluoronaphthalene, 323-09-1; potassium *tert*-butoxide, 865-47-4; *tert*-butyl alcohol, 75-65-0.

The Reaction of Bromonaphthalene with Potassium *tert*-Butoxide and *tert*-Butyl Alcohol in Dimethyl Sulfoxide[1a]

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The reaction of 1-bromonaphthalene with potassium *tert*-butoxide in a *tert*-butyl alcohol-dimethyl sulfoxide mixture has been extensively studied. The major products observed in this reaction were *tert*-butyl 1- and 2-naphthyl ethers (V and VI), 1- and 2-naphthols (XIV and XV), and 1-methylmercapto-2-naphthol (XII). Ten other identifiable products were also observed. The reaction was studied under a variety of conditions and it was observed that the desired ethers (V and VI) were obtained in greater yields when lower base concentration, lower temperatures, and shorter reaction times were employed. The mole per cent ratio of 1-substituted products (V and XIV) to 2-substituted products (VI and XV) was 0.36 ± 0.02 in every case. This ratio plus the fact that 2-bromonaphthalene reacted to give the same products and almost the same ratio (0.34) suggest that 1,2-dehydronaphthalene is an intermediate in this reaction.

The generation of arynes by reacting aryl halides with amide ions has been studied in detail.[2] Cram and coworkers have shown that the elimination of hydrogen bromide from bromobenzene can be effected using potassium *tert*-butoxide and that the reaction is greatly enhanced when dimethyl sulfoxide (DMSO) is used as a solvent.[3] More recently, Cram and Day[4] and Kise and coworkers[5] have found that aryne intermediates reacted with DMSO to yield 2-methylmercaptophenol-type products.

In connection with another study,[6] we have reported the preparation of *tert*-butyl 2-naphthyl ether from the reaction of 1-bromonaphthalene and potassium *tert*-butoxide in a *tert*-butyl alcohol-DMSO mixed solvent. At that time no *tert*-butyl 1-naphthyl ether was found and a mixture of 1- and 2-naphthols was the major product.[6] We now would like to report on the reaction of 1- and 2-bromonaphthalene with potassium *tert*-butoxide in a *tert*-butyl alcohol-DMSO solvent mixture. This reaction not only gave *tert*-butyl 1- and 2-naphthyl ethers and naphthols but also eleven other identifiable products (see Scheme I).

Results

Bromonaphthalene was rapidly added to the potassium *tert*-butoxide-*tert*-butyl alcohol-DMSO mixture at the appropriate temperature. The reaction proved to be exothermic. Upon completion of the reaction, the neutral and naphtholic products (Scheme I) were separated and the products were analyzed by vapor phase chromatography (vpc). The results of several runs are shown in Table I.

The hydrocarbons (I-IV) and naphthols (XIV and XV) were identified by comparing them with authentic compounds. The two *tert*-butyl ethers (V and VI) were identified as previously described[6] and by comparing them with authentic samples prepared by the method of Frisell and Lawesson.[7] The binaphthyls (VII and VIII) were not unequivocally identified; however, authentic samples exhibited the same vpc retention times. Authentic α,α'- and β,β'-dinaphthyl ethers (IX and XI) were prepared from the corresponding naphthols.[8] These authentic samples gave the same vpc retention times as compounds IX and XI. In addition, the product of reacting a mixture of 1- and 2-naphthols with sodium bisulfate at high temperatures[8] exhibited the same infrared spectrum as compounds IX to XI as collected in one combined sample from the vpc.

Compound XII exhibited the same infrared spectrum as that reported by Leysen and Van Rysselberge[9] for 1-methylmercapto-2-naphthol. The infrared band at 3375 cm^{-1} was unaffected by dilution which indicates the presence of a hydroxy group ortho to a methylmercapto group.[4] Compound XIII exhibited infrared and nuclear magnetic resonance spectra which were very similar to those of compound XII. This spectral similarity, as well as the probable source of

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[1] (a) Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer purchased under the National Science Foundation Grant GP-6837; (b) National Defense Education Act Fellow, 1967-1970.

[2] See R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

[3] D. J. Cram, B. Rickborn, and G. R. Knox, *J. Amer. Chem. Soc.*, **82**, 6412 (1960).

[4] D. J. Cram and A. C. Day, *J. Org. Chem.*, **31**, 1227 (1966).

[5] M. Kise, T. Asari, N. Furukawa, and S. Oae, *Chem. Ind.* (*London*), 276 (1967).

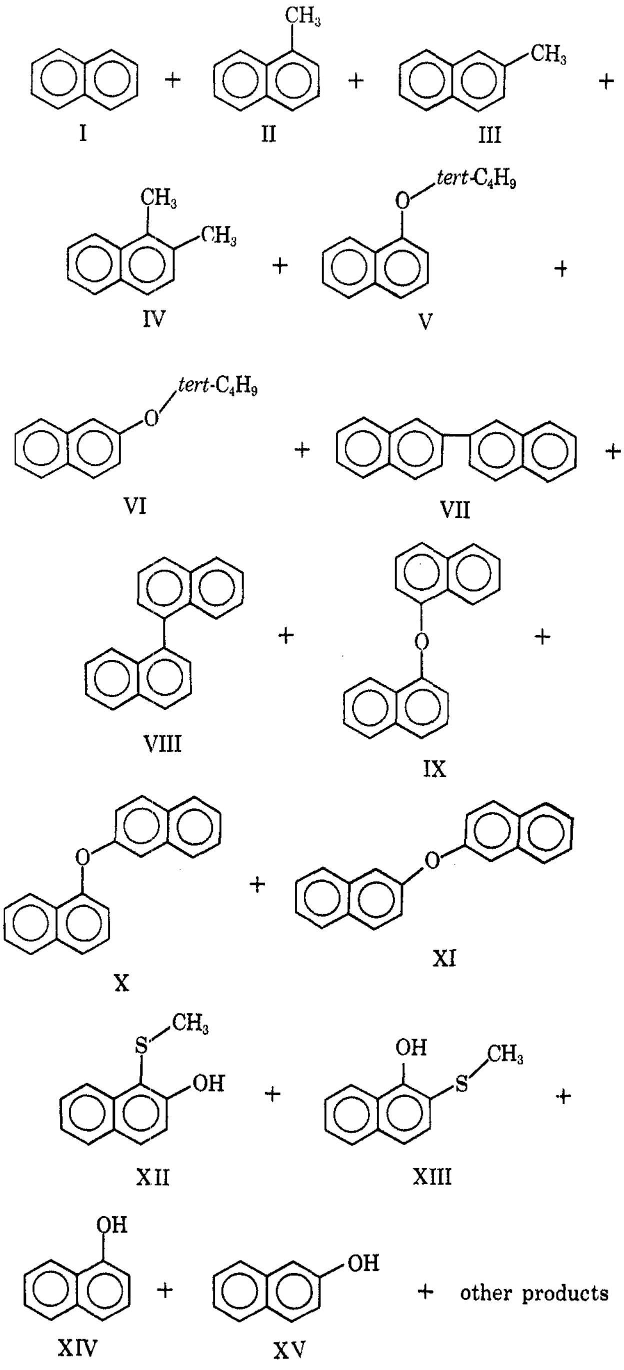
[6] J. S. Bradshaw, N. B. Nielson, and D. P. Rees, *J. Org. Chem.*, **33**, 259 (1968).

[7] C. Frisell and S. O. Lawesson, *Org. Syn.*, **41**, 91 (1961).

[8] W. M. Rodiodow and S. J. Manzow, *J. Soc. Chem. Ind.*, *London*, *Rev. Sect.*, **42**, 509 (1923); see *Chem. Abstr.*, **18**, 981^7 (1924).

[9] R. Leysen and J. Van Rysselberge, *Spectrochim. Acta*, **22**, 777 (1966).

SCHEME I



both XII and XIII, suggests that compound XIII is 2-methylmercapto-1-naphthol.

The first reaction (run 1) was carried out using the conditions employed by Sahyun and Cram[10] for the bromobenzene reaction. In our case it was apparent that the conditions were too severe. When the amount of base was reduced, a much greater yield of the desired ethers (V and VI) was obtained and the yield of naphthols (XIV and XV) was greatly reduced (runs 1 and 2). A similar enhancement of yields was observed at lower temperatures (compare run 7 with run 2).

The higher ether, and correspondingly lower naphthol, yields can be attributed to a greater stability of the ethers in the less severe reaction conditions. We found that the *tert*-butyl naphthyl ethers decomposed to the corresponding naphthols under our reaction conditions. They were, however, much more stable at lower temperatures.

Discussion

On reviewing the results in Table I, it becomes apparent that the same intermediate is leading to the major products in every experiment. The mole per cent ratio of 1-substituted products (V and XIV) to 2-substituted products (VI and XV) is 0.36 ± 0.02 in every case except runs 5 and 6 where either the base concentration is lower or the alcohol was eliminated (Table II). When 2-bromonaphthalene was reacted (run 8, Tables I and II), the mole per cent ratio of 1- and 2-substituted products was, within experimental error, the same as for 1-bromonaphthalene. These results clearly indicate that there is a common intermediate in these reactions. The greater preponderance of evidence concerning this and similar reactions[2-5] has shown the intermediate to be a 1,2-dehydroaromatic compound. In our case, this would be 1,2-dehydronaphthalene.

The ratio of 0.36 for 1 to 2 products is interesting. Most of the previous studies of 1,2-dehydronaphthalene, generated by a variety of methods, exhibited a ratio of 0.5 or higher except in cases where a bulky nucleophile was used.[11] In one case, the 1:2 ratio changed progressively from 0.64 to 0.075 when the base–nucleophile was changed from lithium diethylamide–diethylamine (0.64) to diisobutylamide–diisobutylamine (0.56), diisopropylamide–diisopropylamine (0.15), and dicyclohexylamide–dicyclohexylamine (0.075).[12] Our results indicate that *tert*-butyl alcohol is more bulky than diisobutylamine but less bulky than diisopropylamine. A less bulky alkoxide–alcohol system should give a higher ratio of 1- to 2-substituted products.

In an attempt to test this theory, we treated 1-bromo- and 2-bromonaphthalene with potassium *n*-butoxide in a 1-butanol–DMSO solvent mixture at 140° (same conditions as run 2, Table I). The ratio of 1- to 2-substituted products was 1.24 in the 1-bromonaphthalene reaction and 0.30 in the 2-bromonaphthalene reaction. A considerable amount (up to 28%) of naphthalene was observed in these reactions probably due to reductive processes observed by others.[13,14]

The fact that 1-bromonaphthalene gave the 2-ether and 2-bromonaphthalene gave the 1-ether suggests that at least some of the reaction in both cases is proceeding by a 1,2-dehydronaphthalene mechanism. Coupled with this is a direct nucleophilic substitution mechanism which would give mostly 1-ether from 1-bromonaphthalene and 2-ether from 2-bromonaphthalene.[15] A 2,3-dehydronaphthalene mechanism could also be possible in the reaction of 2-bromonaphthalene in the *n*-butoxide–1-butanol system. Work is in progress to sort out the various mechanisms in the *n*-butoxide system.

In any mechanistic scheme, the base–alcohol–DMSO system cannot be divorced from the intermediate. That

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(10) M. R. V. Sahyun and D. J. Cram, *Org. Syn.*, **45**, 89 (1965).

(11) Reference 2, p 139.

(12) R. Huisgen and L. Zirngibl, *Chem. Ber.*, **91**, 2375 (1958).

(13) J. F. Bunnett and T. K. Brotherton, *J. Amer. Chem. Soc.*, **78**, 6265 (1956).

(14) J. Sauer, R. Huisgen, and A. Hauser, *Chem. Ber.*, **91**, 1461 (1958).

(15) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

TABLE I
RESULTS OF THE REACTION OF 1- AND 2-BROMONAPHTHALENE WITH POTASSIUM *tert*-BUTOXIDE IN *tert*-BUTYL ALCOHOL–DMSO

	Mole ratios				Temp,	Time,		Products[d]			
Run	ArBr	KOR	HOR	DMSO	°C	min	Conversion	I	II	III	IV
1[a,b]	1	4.06	3.38	14.75	140	8	98.2	2.3	0.6	0.2	0.3
2[b]	1	2	3	15	140	8	100	2.3	0.5	0.1	
3[b]	1	2	3	15	140	8	100	2.6	0.5	0.1	
4[b]	1	2	3	15	100	5	86.3	3.0	0.2	0.1	
5[b]	1	1	3	15	100	5	34.2	1.8	0.1		
6[b]	1	2	0	15	100	5	99.9	3.2	1.2	0.2	0.3
7[b]	1	2	3	15	80	15	38.3	1.3			
8[c]	1	2	3	19.1	80	15	72.7	0.6	0.1		

	Products[d]										
Run	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
1	3.9	19.3	0.2	0.1	0.8	3.1	3.0	4.0	1.5	14.4	30.6
2	8.5	27.8	0.2	0.2	0.8	2.7	2.5	7.4	1.1	4.8	8.5
3	8.3	28.1	0.2	0.2	0.8	2.9	2.6	7.7	1.2	5.2	9.7
4	9.1	26.8	0.2	0.2	1.3	4.5	4.2	9.2	0.2	3.0	6.9
5	6.9	17.8	0.3	0.2	0.5	1.4	1.3	14.0	2.5	1.9	4.0
6	3.7	13.6	0.4	0.2	0.7	2.7	4.0	7.9	1.0	5.7	9.3
7	13.5	40.2	0.4	0.1	0.5	1.4	1.5	12.2	1.3	2.4	5.3
8	10.8	31.7	0.3		0.7	1.9	2.1	9.6	0.5	1.1	3.2

[a] Same condition as Sahyun–Cram reaction, see ref 10. [b] 1-Bromonaphthalene. [c] 2-Bromonaphthalene. [d] Mole per cent yields.

TABLE II
MOLE PER CENT RATIO OF 1-SUBSTITUTED PRODUCTS (V AND XIV) TO 2-SUBSTITUTED PRODUCTS (VI AND XV)

Run[a]	Mole per cent ratio (V + XIV:VI + XV)	Run[a]	Mole per cent ratio (V + XIV:VI + XV)
1	0.37	5	0.40
2	0.37	6	0.41
3	0.36	7	0.35
4	0.36	8	0.34

[a] See Table I for conditions.

alcohol is necessary is shown by the fact that without alcohol, a very poor yield of the desired ethers was obtained (see run 6 in Table I). A similar effect was observed by Huisgen and Sauer for the reaction of bromobenzene with lithium piperidide.[16] As they increased the amount of piperidine in the reaction, the overall rate of the reaction increased. They attributed this to a catalytic action of piperidine on the initial metalation step.[16] In our case, it should be a similar type of effect in the initial removal of the proton. 1,2-Dehydronaphthalene, produced in the fast loss of bromide ion, would then add either *tert*-butyl alcohol or more likely *tert*-butoxide ion. This addition is probably influenced by stereochemistry imposed by the peri hydrogen resulting in mostly 2-substituted naphthalene.

The *tert*-butyl ether decomposed in both acid[6] and base. In the base-catalyzed decomposition at higher temperatures, a gas was observed leaving the solution. In the initial experiment to generate 1,2-dehydronaphthalene the evolution of gas was very vigorous. This gas was not collected; however, Cram and Day observed similar results in their system and suggested that isobutylene and the corresponding phenol were formed by a simple elimination process.[4]

The presence of naphthalene in the products of the *tert*-butoxide system is somewhat surprising. This material may be produced by a mechanism similar to that postulated by Bunnett and Victor[17] for the dehalogenation of various trihalobenzenes. They proposed that methylsulfinyl carbanion produced in an equilibrium between *tert*-butoxide and DMSO was undergoing a nucleophilic displacement on the halogen forming an aryl anion.[17,18] The aryl anion then abstracts a proton from the solvent.

$$CH_3SOCH_3 + tert\text{-}C_4H_9O^- \rightleftharpoons CH_3SOCH_2^- + tert\text{-}C_4H_9OH$$

$$CH_3SOCH_2^- + ArBr \longrightarrow CH_3SOCH_2Br + Ar^-$$

$$Ar^- + tert\text{-}C_4H_9OH \longrightarrow ArH + tert\text{-}C_4H_9O^-$$

In an attempt to determine if this mechanism was appropriate for 1-bromonaphthalene, we treated 1-bromonaphthalene with sodium methylsulfinyl carbanion.[19] Only a minor amount of naphthalene (1.3 mol %) was produced in this reaction. The small amount of naphthalene produced when a large amount of the carbanion base was present suggests that the Bunnett–Victor mechanism is not appropriate in the naphthalene system.

The methylnaphthalenes (II–IV) are probably being formed from naphthalene and methylsulfinyl carbanion as reported by Schriesheim and coworkers.[20] They found a ratio of 96% 1-methylnaphthalene to 4% 2-methylnaphthalene when naphthalene was treated with DMSO and potassium *tert*-butoxide in diglyme. We found that under our reaction conditions, naphthalene gave 1- and 2-methylnaphthalene in a similar ratio.

The formation of the dinaphthyl ethers (IX–XI) probably resulted from the reaction of 1- and 2-naphthoxide on 1,2-dehydronaphthalene. Similar results have been reported for the reaction of phenoxide with dehydrobenzene.[21–23]

The methylmercaptonaphthols (XII and XIII) were probably formed by a dipolar addition of DMSO to

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[16] R. Huisgen and J. Sauer, *Chem. Ber.*, **92**, 192 (1959).

[17] J. F. Bunnett and R. R. Victor, *J. Amer. Chem. Soc.*, **90**, 810 (1968).

[18] See also C. G. Cardenas, A. N. Khafaji, C. L. Osborn, and P. D. Gardner, *Chem. Ind. (London)*, 345 (1965).

[19] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

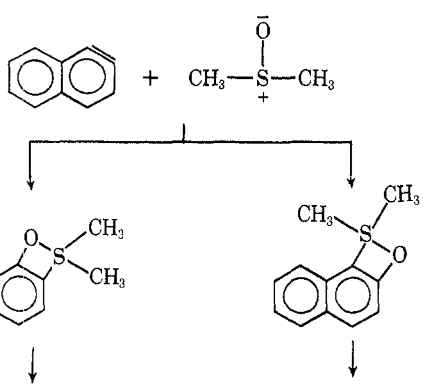
[20] P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, **30**, 3233 (1965).

[21] F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1958).

[22] Von W. Strubell, *J. Prakt. Chem.*, **14**, 60 (1961).

[23] R. W. Hoffmann, *Chem. Ber.*, **97**, 2772 (1964).

1,2-dehydronaphthalene as suggested by Cram and Day[4] and Kise and coworkers.[5] The resulting adduct is believed to eliminate methylene (in the form of polymethylene) to form the observed products.[4,5] The reasons for the observed preponderance of 1-methylmercapto-2-naphthol (XII) over the 2-1 isomer (XIII) is not readily apparent.



XIII XII

Experimental Section

Materials and Apparatus.—1-Bromonaphthalene was used as received from Matheson Coleman and Bell. Potassium *tert*-butoxide was used as received from MSA Research Corp. DMSO (J. T. Baker reagent grade) was passed through silica gel and stored over type 4A molecular sieves (Fisher Scientific Co.). Reagent grade *tert*-butyl alcohol and 1-butanol (Eastman Chemical Co.) were distilled from potassium and stored over type 4A molecular sieves. The naphthalene compounds used to compare with the reaction products were purchased from Aldrich Chemical Co. (naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1-naphthol, and 2-naphthol) and K and K Laboratories (1,2-dimethylnaphthalene, 1,1′-binaphthyl, and 2,2′-binaphthyl). The *tert*-butyl perbenzoate was purchased from K and K Laboratories.

Authentic samples of *tert*-butyl 1-naphthyl ether and *tert*-butyl 2-naphthyl ether were prepared by the method of Frisell and Lawesson[7] using 1- and 2-bromonaphthalene (0.25 mol), magnesium (0.265 g-atom), and *tert*-butyl perbenzoate (0.15 mol). The yield of the *tert*-butyl 1-naphthyl ether was 34%, n^{20}_{D} 1.5759, bp 85–95° (2 mm) [lit.[24] n^{20}_{D} 1.5772, bp 87–88° (0.4 mm)]. The yield of *tert*-butyl 2-naphthyl ether was 67%, n^{20}_{D} 1.5788, bp 95–100° (2 mm) (lit.[6] n^{20}_{D} 1.5769).[6] Naphthalene was a byproduct of these reactions.

1,1′-Dinaphthyl and 2,2′-dinaphthyl ethers were prepared by the procedure of Rodiodow and Manzow[8] from the 1- and 2-naphthols and sodium bisulfate. 2,2′-Dinaphthyl ether (40% yield) was purified by sublimation, mp 97.5–100.5° (lit.[25] mp 105°). 1,1′-Dinaphthyl ether (64% yield) was purified by recrystallization from 95% ethanol, mp 106–106.5° (lit.[25] mp 110°).

All reaction runs were analyzed and where possible the products were isolated using a Varian Aerograph 202-B temperature programming vapor phase chromatograph (vpc). All infrared (ir) spectra were obtained on a Perkin-Elmer 457 spectrophotometer. A Varian A-60A spectrometer[1a] was used to obtain the nuclear magnetic resonance (nmr) spectra.

Reaction of 1-Bromonaphthalene and Base (Run 1).—A mixture of 25 ml (0.3525 mol) of DMSO, 7.62 ml (5.99 g, 0.0808 mol) of *tert*-butyl alcohol, and 11.84 g (0.0970 mol) of potassium *tert*-butoxide was placed in a dry 100-ml three-necked round-bottom flask equipped with a thermometer, reflux condenser, and an addition funnel. A 1000-ml round-bottom flask with a male joint on the bottom was placed between the reaction vessel and the condenser. The potassium *tert*-butoxide dissolved when the stirred (magnetic stirring bar) reaction mixture was heated to 140°. 1-Bromonaphthalene (4.94 g, 0.0239 mol) was quickly added by means of the addition funnel. The reaction mixture turned black and vigorously foamed into the 1000-ml flask and condenser. After 8 min, the reaction mixture was added to 115 ml of ice water. The aqueous mixture was saturated with sodium chloride and extracted four times with 100-ml portions of ethyl ether. The combined ether extracts were washed with an aqueous 5% sodium hydroxide solution and dried over anhydrous magnesium sulfate. After the drying agent was filtered, the ether extract was evaporated leaving 2.11 g of a dark brown semisolid. This material was the neutral fraction.

The remaining aqueous DMSO reaction mixture was acidified to a pH of 1 with concentrated hydrochloric acid and extracted four times with 100-ml portions of ether. The combined ether extracts were washed with water and dried over anhydrous magnesium sulfate. After the drying agent was filtered, the ether extract was evaporated leaving 1.79 g of a dark yellow-green solid. This material was the acidic fraction.

The other reactions (runs 2–8, Table I) were carried out in the same manner using the listed ratios of reactants and solvents and the appropriate conditions. The reaction using potassium *n*-butoxide and 1-butanol was carried out by dissolving the required amount of potassium metal in enough 1-butanol to obtain a ratio of 2 mol of potassium *n*-butoxide to 3 mol of 1-butanol. The DMSO was then added and the reaction carried out as reported above. The analysis for all experiments was carried out as described below.

Analysis of the Neutral Fraction.—The neutral fraction was dissolved in 5 ml of benzene and subjected to vpc analysis using 1-bromo-4-methylnaphthalene as an internal standard.[26] The starting 1-bromonaphthalene was found to contain a minute amount of naphthalene. This was subtracted from the amount found in the products. The lower boiling compounds (V–VI) were analyzed on a 5 ft by $^1/_8$ in. column packed with a mixture of 1% SE-30 and 1% Carbowax 20M on 60–80 mesh, Chromosorb G, acid washed, at 115°. The higher boiling fractions (VII–XI) were analyzed on a 5 ft by $^1/_8$ in. column packed with 1.5% poly-*m*-phenoxylene (PMPE) on 80–100 mesh Varaport 30 using a program from 125 to 290° at a rate of 10° per min. A total of 27 peaks were observed. The retention times for compounds I–XI were compared with authentic samples of those compounds. Total amounts and yields were determined by the internal standard method.[26] Results are listed in Table I.

All the compounds in the neutral fraction except III, VII, and VIII were isolated from the vpc using a 5 ft by 0.25 in. column packed with 20% Carbowax 20M on 60–80 mesh, Chromosorb G, acid washed, for the lower boiling fraction and 1.5% PMPE on 80–100 mesh Varaport 30 for the higher boiling fraction. The compounds in the lower boiling fraction all exhibited ir spectra which were identical with those of authentic samples. Compounds IX–XI were isolated together and exhibited an ir spectrum which was exactly the same as that for an authentic sample prepared by reacting a mixture of 1- and 2-naphthols with sodium bisulfate.[8]

The *n*-butyl 1-naphthyl and *n*-butyl 2-naphthyl ethers exhibited ir and nmr spectra which were consistent with their assigned structures. The 2-substituted ether was also identical with that prepared previously.[6]

Analysis of the Acidic Fraction.—The acidic fraction (XII–XV) was dissolved in 3 ml of anhydrous ether and subjected to vpc analysis using a 5 ft by $^1/_8$ in. column packed with a mixture of 1% SE-30 and 1% Carbowax 20M on 60–80 mesh, Chromosorb G, acid washed, at 175°. Five peaks were observed. The ir spectrum of the total material collected from the vpc was the same as the crude solid before it was subjected to analysis. Therefore, no internal standard was used; the area of each peak was used to determine the amount of that particular product. Results are listed in Table I.

Four of the five peaks were isolated from the vpc using a 5 ft by 0.25 in. column packed with 20% Carbowax 20M on 60–80 mesh, Chromosorb G, acid washed. Peak 2 exhibited an ir spectrum which was the same as that reported for 1-methylmercapto-2-naphthol (compound XII).[9]

Anal. Calcd for $C_{11}H_{10}OS$: C, 69.44; H, 5.30. Found: C, 69.30; H, 5.34.

Peak 3 exhibited the following major ir bands: 3385, 3060, 2925, 1629, 1621, 1590, 1573, 1506, 1460, 1438, 1390, 1360, 1320, 1268, 1249, 1205, 1153, 1136, 1073, 972, 886, 855, 808, 785, 778, 750, 724, and 668 cm^{-1}. The nmr spectrum had peaks at δ 7.76 (m, 6), 3.54 (s, 1), and 2.33 (s, 3). The ir spectrum was

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[24] S. O. Lawesson, *J. Amer. Chem. Soc.*, **81**, 4230 (1959).

[25] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969–1970, p C-294.

[26] A. B. Littlewood, "Gas Chromatography, Principles, Techniques and Applications," Academic Press, New York, N. Y., 1962, p 246.

similar to that of vpc peak 2 (compound XII) and the nmr spectrum was identical. On this basis, peak 3 was believed to be 2-methylmercapto-1-naphthol (XIII). Not enough of this compound could be isolated for a carbon-hydrogen analysis. Vpc peaks 4 and 5 exhibited ir spectra which were identical with those of 1- and 2-naphthols, respectively.

Decomposition of *tert*-Butyl 1-Naphthyl Ether.—Mixtures of potassium *tert*-butoxide, *tert*-butyl alcohol, and DMSO of the appropriate ratio (same as in Table I) were heated to the desired temperature in a dry three-necked round-bottom flask equipped with a thermometer, addition tube, and condenser. *tert*-Butyl 1-naphthyl ether was added at once through the addition tube. After the desired reaction time, the reaction mixture was added to cold water and worked up as described above for the 1-bromonaphthalene reaction. The neutral and acidic fractions were analyzed as described above. In every case the ether decomposed to the naphthol. At high temperature only 5–10% of the ether was recovered; the other 90–95% was the naphthol. At lower temperatures (80–100°) most (60%) of the ether was recovered.

Reaction of Naphthalene with the Base–DMSO Solution.—Naphthalene (0.13 g, 0.001 mol) was added to a solution of 25 ml (27.5 g, 0.35 mol) of DMSO, 6.0 g (0.08 mol) of *tert*-butyl alcohol, and 11.8 g (0.10 mol) of potassium *tert*-butoxide at 140°. After 40 min, the reaction was added to ice water and worked up as reported above for the 1-bromonaphthalene reaction. No acidic fraction was observed. The neutral fraction was analyzed as reported above to yield 47.3% recovered naphthalene, 7.6% 1-methylnaphthalene, and 0.6% 2-methylnaphthalene. No 1,2-dimethylnaphthalene was observed.

Reaction of Methylsulfinyl Carbanion with 1-Bromonaphthalene.—Methylsulfinyl carbanion was prepared according to the procedure of Corey and Chaykovsky[19] from 124.83 g (1.6 mol) of DMSO and 4.5 g (0.19 mol) of sodium hydride. This mixture was placed in a dry 500-ml three-necked round-bottom flask equipped with a thermometer, condenser, addition funnel, and magnetic stirring. The temperature was raised to 80° and 19.5 g (0.09 mol) of 1-bromonaphthalene was added at once. The reaction mixture immediately turned black and the temperature rapidly increased to 150°. After 15 min (the temperature had lowered to 104°), the mixture was added to ice water and worked up as reported above. The acidic fraction was analyzed as reported above to yield 3.8% XII, 1.3% XIII, 0.3% XIV, and 0.5% XV. The neutral fraction yielded (analyzed as reported above) 1.3% I, 2.7% III, and 0.3% II. Another compound (11.4%) was observed and isolated. The nmr spectra of this compound was the same as that reported by Zweig and coworkers[27] for 1-methylthionaphthalene. The ir spectrum was consistent with this structure.

Anal. Calcd for $C_{11}H_{10}S$: C, 75.81; H, 5.79. Found: C, 75.94; H, 5.63.

Registry No.—1-Bromonaphthalene, 90-11-9; 2-bromonaphthalene, 580-13-2; potassium *tert*-butoxide, 865-47-4.

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The Chemistry of Thiolsulfonates and Related Derivatives. Nucleophilic Reactions on Sulfenyl Sulfur[1a]

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The reaction of thiolsulfonates with aminophosphines proceeds by nucleophilic attack on sulfenyl sulfur giving rise to sulfones and sulfinate esters as reaction products. This is in marked contrast to the reaction of triphenylphosphine (**3**) with thiolsulfonates where deoxygenation is observed. This dichotomy does not extend to the corresponding reaction of phosphines with sulfenylthiolsulfonates. Here, nucleophilic attack on sulfenyl sulfur is observed for both triphenylphosphine (**3**) and tris(diethylamino)phosphine (**4**). In addition, the desulfurization of cyclic thiosulfonates provides a new, general route to cyclic sulfinate esters.

As part of our continuing investigation of nucleophilic displacements on sulfenyl sulfur we have examined the reaction of a number of thiolsulfonates **1** and sulfenyl thiolsulfonates **2** with various trivalent phosphorus derivatives.

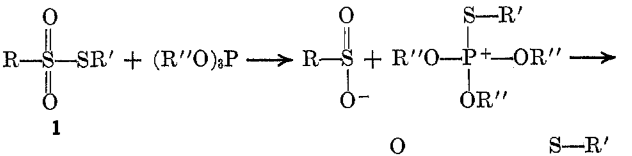
RSO_2SR **1** RSO_2SSR **2**

The behavior of trivalent phosphorus compounds toward disulfides and trisulfides has been shown to be a function of the type of substitution on the phosphorus atom (aminophosphines,[2,3] alkylphosphines,[3] arylphosphines,[3,4] and phosphites).[5]

Thiolsulfonates have been reported to undergo deoxygenation with triphenylphosphine[6] (**3**) or desulfurization with trialkyl phosphites.[7] In the latter reaction, the

$$R{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}SR + 2Ph_3P \longrightarrow RSSR + 2Ph_3P{=}O$$

1 **3**



$$R{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}SR' + (R''O)_3P \longrightarrow R{-}\overset{O}{\underset{O^-}{\overset{\|}{\underset{|}{S}}}} + R''O{-}\overset{S-R'}{\underset{OR''}{\overset{|}{\underset{|}{P^+}}}}{-}OR'' \longrightarrow$$

1

$$R{-}\overset{O}{\overset{\|}{S}}{-}OR'' + O{=}\overset{S-R'}{\overset{|}{P}}(OR'')_2$$

sulfinate anion, presumably formed by nucleophilic displacement on sulfenyl sulfur, may react through oxygen to afford sulfinate esters or through sulfur to give sulfones. However, only products resulting from O-alkylation in an Arbusov-like rearrangement[8] are ob-

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