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

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The reaction of monoiodo-, monochloro-, and monofluoronaphthalenes with potassium *tert*-butoxide in a *tert*-butyl alcohol–dimethyl sulfoxide medium at 140° has been examined; the results are compared to the reaction of the monobromonaphthalenes under the same conditions. The major products observed in the bromo-, iodo-, and chloronaphthalene reactions were 1- and 2-*tert*-butyl naphthyl ethers (IV and V), 1- and 2-naphthols (XIII and XIV), and 1-methylmercapto-2-naphthol (XI). Other products were found in minor yields. The mole per cent ratio of 1-substituted products (IV and XIII) to 2-substituted products (V and XIV) was found to be 0.35 ± 0.03 in every case suggesting that 1,2-dehydronaphthalene is an intermediate in each of these reactions. The fluoronaphthalenes were found to undergo only direct nucleophilic substitution with no formation of 1,2-dehydronaphthalene. The order of addition of potassium *tert*-butoxide and *tert*-butyl alcohol to DMSO seems to be critical in this reaction. When *tert*-butoxide is added first, the major products are not compounds IV, V, XI, XIII, and XIV, but are 1- and 2-methylthionaphthalene (XV and XVI).

Bromobenzene is known to react with potassium *tert*-butoxide to form *tert*-butyl phenyl ether by way of an aryne mechanism.[2-4] In another paper,[5] we report the reaction of 1- and 2-bromonaphthalene with potassium *tert*-butoxide in a *tert*-butyl alcohol–dimethyl sulfoxide mixture.[6] We found that the major products formed in this reaction were 1- and 2-*tert*-butyl naphthyl ethers (IV and V), 1- and 2-naphthols (XIII and XIV), and 1-methylmercapto-2-naphthol (XI). Ten other identifiable products were also observed. The reaction was studied under a variety of conditions and it was found that the ethers were formed in higher yields when less base concentration, lower temperature, and shorter reaction times were used. This was a result of the base-catalyzed decomposition of the ethers to give the corresponding naphthols and isobutylene under the reaction conditions. Maximum yields of the ethers were obtained at 80° with a molar ratio of 1:2:3:15 for the following reactants: bromonaphthalene–potassium *tert*-butoxide–*tert*-butyl alcohol–DMSO.[5] The mole per cent ratio of 1-substituted products to 2-substituted products was found to be 0.36 ± 0.02 under all conditions except when the initial concentration of base was greatly reduced or when the initial concentration of alcohol was eliminated. The fact that this ratio was obtained with both 1- and 2-bromonaphthalene indicated that 1,2-dehydronaphthalene was an intermediate in that reaction.[5]

We now report on the reaction of 1- and 2-iodo-, -chloro-, and -fluoronaphthalenes with potassium *tert*-butoxide in a *tert*-butyl alcohol–DMSO solvent mixture and compare the results found with those of the bromonaphthalene reaction.[5] The iodo- and chloronaphthalene reactions were found to be very similar to the bromonaphthalene reactions. However, the fluoronaphthalene reactions were found to proceed by way of direct nucleophilic substitution rather than the aryne mechanism.

Results

The halonaphthalene was rapidly added to the potassium *tert*-butoxide–*tert*-butyl alcohol–DMSO mixture maintained at 140°. The 1-halonaphthalene compounds were added as the neat liquids while a DMSO solution of the solid 2-halonaphthalene compounds was used. The reactions with the bromo- and iodonaphthalenes were more exothermic than those with the chloro- and fluoronaphthalenes. After 8 min, the reaction mixture was added to water and the neutral products (I–X in Scheme I) and acidic products (XI–XIV in Scheme I) were separated by extraction with ether and analyzed by vapor phase chromatography (vpc) as described previously.[5]

The results of the various runs are shown in Table I. Runs 1 and 2 are from ref 5 and are reproduced here to compare with runs 3–9. Although our previous work[5] showed that the conditions for maximum yield of the *tert*-butyl naphthyl ethers (IV and V) from 1-bromonaphthalene was at 80°, an initial reaction of 1-chloronaphthalene at 80° showed only a trace of ether formation. Therefore, all runs were made at 140° for comparison purposes. Even at this temperature only an 86% conversion was observed for the chloronaphthalenes with a lower conversion taking place for the fluoronaphthalenes.

Table I shows that a particular set of reaction conditions which maximize the yield of ethers (IV + V) over naphthols (XIII + XIV) produced from one halonaphthalene do not show the same result with other halonaphthalenes (compare runs 1–4 with 5–9). The formation of naphthols XIII and XIV is presumed in each case to be from the base-catalyzed decomposition of ethers IV and V.[5]

All products I–XIV (Scheme 1) were identified as described previously.[5] In addition to these, two additional products were observed in the 1-chloronaphthalene reaction (run 6). They were identified as 1-methylthionaphthalene (XV), 1.0%, and 2-methylthionaphthalene (XVI), 0.5%, from their nmr spectra, which matched exactly those given by Zweig and coworkers,[8] and from their ir spectra which were consis-

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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. (c) To whom inquiries should be addressed.

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

[3] J. I. G. Cadogan, J. K. A. Hall, and J. T. Sharp, *J. Chem. Soc. C*, 1860 (1967).

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

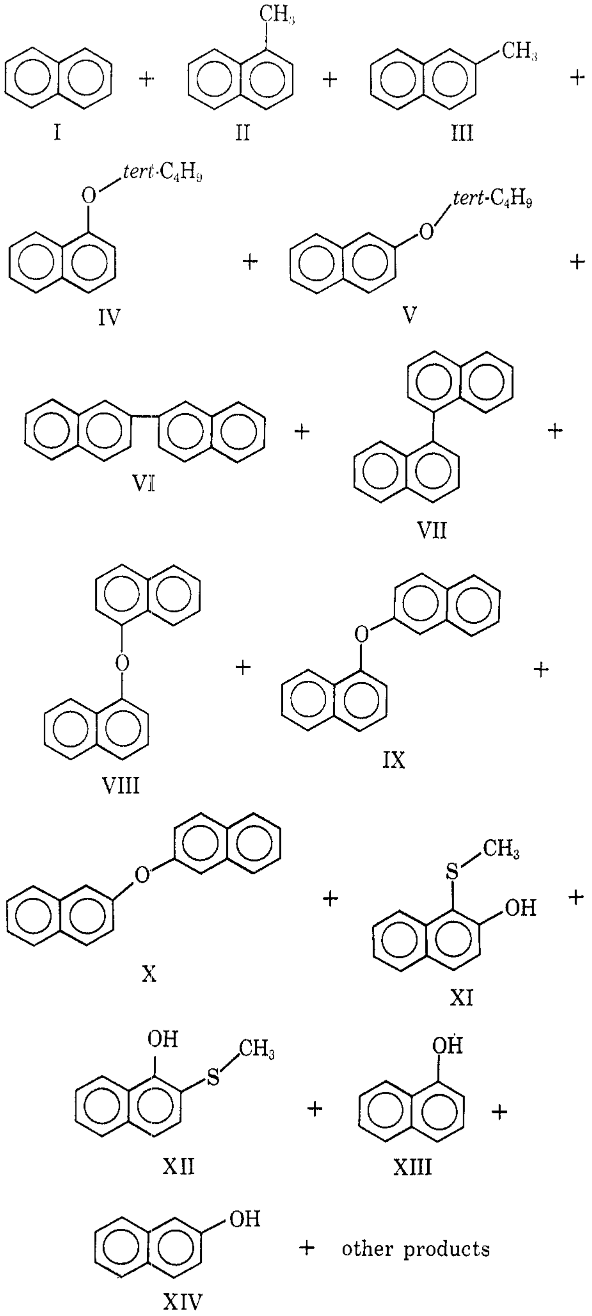
[5] J. S. Bradshaw and R. H. Hales, *J. Org. Chem.*, **36**, 318 (1971).

[6] We used the procedure of Sahyun and Cram.[7]

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

[8] A. Zweig, J. E. Lancaster, and M. T. Negia, *Tetrahedron*, **23**, 2577 (1967).

SCHEME I



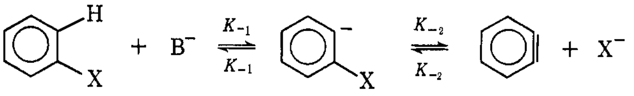
tent with these structures. In addition, compound XV was found to be identical with 1-methylthionaphthalene which was isolated from the reaction of methylsulfinyl carbanion with 1-bromonaphthalene.[5] Compounds XV and XVI were not noticed in any other run except run 7 where only trace amounts were formed. However, in a preliminary run with 1-chloronaphthalene, greater yields of compounds XV and XVI were produced (6.4 and 2.9%, respectively) while only small amounts of ethers IV and V (total 1.6%) and naphthols XIII and XIV (total 9.4%) were formed.

Upon examination of the experimental procedure of these two experiments (run 6, Table I, and the preliminary 1-chloro run), it was determined that both reactions were run exactly the same except for one point. In the preliminary run, the potassium *tert*-butoxide was added to hot DMSO. After the *tert*-butoxide dissolved, the *tert*-butyl alcohol was added and the temperature raised to 140°. In run 6 (Table I), the *tert*-butyl alcohol was added first to the hot DMSO followed by addition of potassium *tert*-butoxide. When both the 1-bromonaphthalene and 2-iodonaphthalene experiments were repeated with potassium *tert*-butoxide being added *before tert*-butyl alcohol, similar results were found in that the major neutral fraction products were compounds XV and XVI.

Discussion

The mole per cent ratio of 1-substituted products (IV and XIII) to 2-substituted products (V and XIV) of 0.36 ± 0.02 found previously[5] for 1-bromonaphthalene under a variety of conditions indicated that these products were being formed through a 1,2-dehydronaphthalene intermediate. The fact that a ratio of 0.34 was found for 2-bromonaphthalene at 80° confirmed this deduction.[5] From Table II we see that the mole per cent ratio of 1-substituted products to 2-substituted products at 140° is 0.35 ± 0.03 for not only the 1- and 2-bromonaphthalene reactions, but also for the 1- and 2-iodonaphthalene and 1- and 2-chloronaphthalene reactions as well. This value is within experimental error of that obtained previously[5] and would indicate that 1,2-dehydronaphthalene is indeed an intermediate in the reaction of the monohalonaphthalenes with potassium *tert*-butoxide in a *tert*-butyl alcohol–DMSO medium when the halogen is either chlorine, bromine, or iodine.

The fact that the bromo- and iodonaphthalenes are more reactive than the chloronaphthalenes under our experimental conditions (100% conversion compared to 86% conversion) is to be expected in view of the mechanism proposed for the generation of dehydrobenzene from aryl halides.[5,9] In the simplified representation shown below for the formation of dehydrobenzene from



an aryl halide by means of the 2-halophenyl anion, the order of reactivity in K_1 should be F > Cl > Br > I, because the removal of the ortho hydrogen would be enhanced by the increased electronegative properties in going from iodine to fluorine. The order of reactivity for K_2, however, is known to be I > Br > Cl > F.[10] Step 1 is normally assumed to be the rate-determining step due to the extreme instability of the 2-halophenyl anion. However, as soon as step 1 becomes reversible, *e.g.*, when operating in a protic medium, the ratio $K_2/(K_2 + K_{-1}[\mathrm{BH}])$ codetermines the rate.[11] When $K_2 < K_{-1}[\mathrm{BH}]$, K_2 may become rate determining. For the amination of aryl halides in liquid ammonia the two opposing halogen reactivity sequences for K_1 and K_2 are superimposed[12] and the resulting order of reactivity of halobenzenes and 3-halotoluenes were found to be $C_6H_5Br–C_6H_5I–C_6H_5Cl = 20:8:1$[13] and $CH_3C_6H_4Br–CH_3C_6H_4I–CH_3C_6H_4Cl = 13.5:5:1$[14] with the corre-

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[9] R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 58.

[10] Reference 9, p 43.

[11] Reference 9, p 15.

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

[13] F. W. Bergstrom, R. E. Wright, C. Chandler, and W. A. Gilkey, *J. Org. Chem.*, **1**, 170 (1936).

[14] F. W. Bergstrom and C. H. Horning, *ibid.*, **11**, 334 (1946).

TABLE I

RESULTS OF THE REACTION OF 1- AND 2-HALONAPHTHALENE WITH POTASSIUM *tert*-BUTOXIDE IN *tert*-BUTYL ALCOHOL–DMSO AT 140° FOR 8 MIN[a]

Run	ArX	Conversion	Products[c]						
			I	II	III	IV	V	VI	VII
1[b]	1-Br	100	2.3	0.5	0.1	8.5	27.8	0.2	0.2
2[b]	1-Br	100	2.6	0.5	0.1	8.3	28.1	0.2	0.2
3	2-Br	100	1.0	0.4	<0.1	6.2	27.5	0.1	<0.1
4	1-I	100	4.6	0.2	<0.1	8.8	25.5	0.1	0.2
5	2-I	100	2.2	0.1	<0.1	5.6	14.4	0.2	<0.1
6	1-Cl	86.0	6.5	1.5	<0.1	2.1	9.8	0.1	0.3
7	2-Cl	85.6	4.2	1.4	<0.1	1.9	9.1	0.3	0.1
8	1-F	80.3		0.5	<0.1	39.6			
9	2-F	72.8		0.5	<0.1		48.3		

Run	Products[c]						
	VIII	IX	X	XI	XII	XIII	XIV
1	0.8	2.7	2.5	7.4	1.1	4.8	8.5
2	0.8	2.9	2.6	7.7	1.2	5.2	9.7
3	0.8	2.8	2.8	6.1	1.4	6.2	10.6
4	0.8	2.8	2.4	8.6	1.6	2.4	6.2
5	3.0	3.6	3.3	10.6	1.2	6.0	18.1
6	1.1	3.6	2.8	5.6	0.9	6.1	13.9
7	1.6	2.8	2.6	4.7	1.4	5.3	13.4
8						58.3	
9							49.6

[a] Molar ratio of ArX–KO-*tert*-C_4H_9–HO-*tert*-C_4H_9–DMSO is 1:2:3:15 in each case. [b] From ref 5. [c] Mol % yields.

TABLE II

MOLE PER CENT RATIO OF 1-SUBSTITUTED PRODUCTS (IV AND XIII) TO 2-SUBSTITUTED PRODUCTS (V AND XIV)

Run[a]	Mole per cent ratio (IV + XIII/V + XIV)
1	0.37
2	0.36
3	0.33
4	0.35
5	0.36
6	0.35
7	0.32
8	Only 1
9	Only 2

[a] See Table I for reaction conditions and halonaphthalene used.

sponding fluoro compounds being inert. Although a difference between iodonaphthalene and bromonaphthalene could not be observed in our case, chloronaphthalene was much less reactive. This indicates that the presence of *tert*-butyl alcohol in our reaction mixture must have a similar effect in our reaction.

The fact that only *tert*-butyl 1-naphthyl ether and 1-naphthol were found in run 8 (Table I) and *tert*-butyl 2-naphthyl ether and 2-naphthol were found in run 9 (Table I) indicates that only a direct nucleophilic substitution mechanism takes place in the case of the fluoronaphthalenes. Apparently, step 2, in the mechanism shown above, is very much less than −1 when X = F, and the presence of *tert*-butyl alcohol in the reaction mixture reverses the metalation step and enhances the chance for direct substitution. This effect was observed in the reaction of lithium piperidide in ether with both 1-fluoronaphthalene and 1-fluoro-4-methylnaphthalene.[15,16] The mechanism of the reactions was seen to change from complete aryne mechanism to a predominance of nucleophilic substitution as the concentration of piperidine was increased from zero. In our system, the initial *tert*-butyl alcohol is causing only nucleophilic substitution to take place. Cram and coworkers[2] found that the reaction of *o*-fluorotoluene with potassium *tert*-butoxide in DMSO at 100° produced *o*-cresol which contained less than 3% *m*-cresol while *o*-bromotoluene produced a mixture of four parts of *m*-cresol to one part of *o*-cresol. It appears that the reaction of monofluoronaphthalene with potassium *tert*-butoxide in a *tert*-butyl alcohol–DMSO medium is a very good procedure for preparing pure *tert*-butyl 1- and 2-naphthyl ethers. Studies are presently being carried out on the reaction of monofluoronaphthalenes with other alkoxide–alcohol systems, as well as with mercaptide–mercaptan systems, in DMSO to determine the generality of this procedure.

The yields of naphthalene (I, Table I), methylnaphthalenes (II and III), binaphthyls (VI and VII), dinaphthyl ethers (VIII, IX, and X), and methylthionaphthols (XI and XII) were found to be very similar in the iodo- and chloronaphthalene reactions (runs 4–7) as compared to the bromonaphthalene reactions (runs 1–3).[17] Only a small amount of 1- and 2-methylnaphthalenes were found in the fluoronaphthalene runs (run 8 and 9, Table I). The presence of naphthalene in either the fluoronaphthalenes used as starting materials or those recovered from runs 8 and 9 (Table I) could not be determined by vpc analysis because a column could not be found which would separate naphthalene from 1- and 2-fluoronaphthalene. However, an ir spectrum of either the starting materials or the recovered fluoronaphthalenes did not show any naphthalene to be present.

Naphthalene was believed to be produced by the action of methylsulfinyl carbanion on the halonaphthalene to form naphthyl anion.[5,18] The fact that more naphthalene was formed from the reaction of the 1-halonaphthalenes than from that of the 2-halonaphthalenes (compare runs 1, 2, 4, and 6 with 3, 5, and 7, Table I)

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

[16] R. Huisgen, J. Sauer, W. Mack, and I. Ziegler, *ibid.*, **92**, 441 (1959).

[17] For a brief discussion of the mechanism of formation of these products, see ref 5.

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

when the halogen was Cl, Br, or I would lend support for the mechanism which involves an intermediate aryl anion.[5] Shatenshtein has reported that naphthalene underwent a base-catalyzed deuterium exchange reaction in the 1 position more than twice as fast as the 2 position.[19] Similar results were observed in the detritiation of naphthalene.[20] Thus, the 1-naphthyl anion is more stable than the 2 anion.

Apparently, the order of mixing of the solvent, alcohol, and base in these reactions is critical. When the potassium *tert*-butoxide is added first to the hot DMSO followed by addition of the *tert*-butyl alcohol the major neutral fraction products are 1- and 2-methylthionaphthalenes (XV and XVI). The ratio of compound XV to compound XVI under these conditions was 2.21 when 1-chloronaphthalene was used, 1.09 when 1-bromonaphthalene was used, and 0.34 when 2-iodonaphthalene was used. These α/β ratios indicate that compounds XV and XVI are being formed through both a 1,2-dehydronaphthalene and a direct nucleophilic substitution mechanism as was the case with the reactions of potassium *n*-butoxide and *n*-butyl alcohol with monobromonaphthalene.[5] The normal ratio of 1- and 2-substituted products from the 1,2-dehydronaphthalene mechanism is 0.50.[21]

The following mechanism is proposed to account for the above observations.

$$\textit{tert}\text{-}C_4H_9O^- + CH_3SOCH_3 \rightleftharpoons \textit{tert}\text{-}C_4H_9OH + CH_3SOCH_2^- \quad (1)$$

$$CH_3SOCH_2^- \longrightarrow CH_2 + CH_3SO^- \quad (2)$$

$$2CH_3SO^- \rightleftharpoons CH_3S^- + CH_3SO_2^- \quad (3)$$

$$CH_3S^- + C_{10}H_6 \xrightarrow{H^+} 1\text{-}CH_3SC_{10}H_7\ (2\text{-}CH_3SC_{10}H_7) \quad (4)$$

$$CH_3S^- + C_{10}H_7X \longrightarrow CH_3SC_{10}H_7 + X^- \quad (5)$$

The reaction of *tert*-butoxide with DMSO to form the methylsulfinyl carbanion (step 1) is amply precedented.[22,23] This step would occur much faster when no *tert*-butyl alcohol was initially present, *i.e.*, when *tert*-butoxide was added to the DMSO first. The thermal decomposition of the methylsulfinyl carbanion at temperatures above 80° in dimethyl sulfoxide has been shown to form the sulfenate ion (step 2) which disproportionates to the corresponding mercaptide and sulfinate ions (step 3).[24] The methyl mercaptide, being more basic than either of the other ions,[24] then reacts with either 1,2-dehydronaphthalene to give both XV and XVI (step 4) or with the halonaphthalene by direct nucleophilic substitution to give either XV or XVI (step 5). Both 2,4-dinitrochlorobenzene[25] and 1-bromonaphthalene[26] have been postulated to undergo nucleophilic substitution by decomposition products of DMSO to give the corresponding methylthio compounds. The fact that the ratio of 1- to 2-substituted methylthionaphthalenes is larger when 1-chloronaphthalene (2.21) was reacted than when 1-bromonaphthalene (1.09) was reacted indicates that more nucleophilic substitution took place with 1-chloronaphthalene than with 1-bromonaphthalene. This is consistent with the order of reactivity of activated aryl halides in nucleophilic substitution of F ≫ Cl > Br > I found in previous studies. This order was found when *o*- and *p*-nitrophenyl halides and 2,4-dinitrophenyl halides were reacted with sodium methoxide in methanol,[27] when *p*-nitrophenyl halides were reacted with sodium ethoxide in ethanol,[28] when 2,4-dinitrophenyl halides were reacted with ammonia in methanol,[29] and when 2,4-dinitrophenyl halides were reacted with amines in dimethylformamide.[30] This mechanism also accounts for the fact that the major product found by us in the reaction of methylsulfinyl carbanion with 1-bromonaphthalene was 1-methylthionaphthalene (XV).[5]

Experimental Section

Materials and Apparatus.—The following halonaphthalenes were obtained from the sources indicated and were used without further purification: 1-bromonaphthalene, Matheson Coleman and Bell; 2-bromo-, 1-chloro, 1-fluoro- and 1-iodonaphthalenes, Eastman Organic Chemicals; 2-chloronaphthalene, J. T. Baker Chemical Co.; 2-fluoronaphthalene, Aldrich Chemical Co.; and 2-iodonaphthalene, K and K Laboratories. 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 (Eastman Chemical Co.) was distilled from potassium and stored over type 4A molecular sieves.

Authentic samples of the naphthalene compounds used to compare with the reaction products were either obtained commercially or synthesized in our laboratory as explained in our accompanying paper.[5] All reaction runs were analyzed on either a Varian Aerograph 202-B or 1720 temperature programming vapor phase chromatograph. Where possible, products were isolated on a Varian Aerograph 90-P3 vapor phase chromatograph. All infrared (ir) spectra were obtained on a Perkin-Elmer 457 spectrophotometer. A Varian A-60A spectrometer was used to obtain the nuclear magnetic resonance (nmr) spectra.[1a]

The Reaction of Halonaphthalene and Base.—All runs were carried out using the procedure as described in our accompanying paper[5] for the reaction of 1-bromonaphthalene. The molar ratio of halonaphthalene–potassium *tert*-butoxide–*tert*-butyl alcohol–DMSO was 0.025:0.050:0.075:0.375, or 1:2:3:15, in each case. The work-up procedure was carried out exactly as described.[5]

Analysis of Products.—The neutral fraction products (I–X, XV, and XVI) were analyzed as described.[5] Results are listed in Table I. The retention times for compounds I–X 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). Compounds IV, V, XV, and XVI, as well as the recovered starting material from runs 6–9, were isolated from the vpc using a 5 ft by 0.25 in. column packed with 6% SE-30 and 6% Carbowax 20M on 60–80 mesh, acid washed Chromosorb G at 200–220°. Compound XV exhibited ir and nmr spectra identical with those for 1-methylthionaphthalene isolated from the reaction of methylsulfinyl carbanion with 1-bromonaphthalene.[5] Compound XVI exhibited an ir spectrum very similar to that for compound XV except that the bands characteristic for β-substituted naphthalenes were observed at 742 and 810 cm^{-1}. Compound XV exhibited bands characteristic for α substituted naphthalenes at 772 and 790 cm^{-1}. Also, the nmr spectrum of compound XVI,

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[19] See A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 182 (1963).

[20] A. Streitwieser, Jr., and R. G. Lawler, *J. Amer. Chem. Soc.*, **85**, 2854 (1963).

[21] J. F. Bunnett and T. K. Brotherton, *ibid.*, **78**, 155, 6265 (1956).

[22] G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

[23] J. I. Brauman and N. J. Nelson, *J. Amer. Chem. Soc.*, **88**, 2332 (1966).

[24] C. C. Price and T. Yukuta, *J. Org. Chem.*, **34**, 2504 (1969).

[25] G. C. Finger and C. W. Kruse, *J. Amer. Chem. Soc.*, **78**, 6034 (1956).

[26] R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1108 (1964).

[27] B. A. Bolto, J. Miller, and V. A. Williams, *ibid.*, 2926 (1955); G. P. Briner, J. Miller, M. Liveris, and P. G. Lutz, *ibid.*, 1265 (1954); A. L. Beckwith, J. Miller, and G. D. Leahy, *ibid.*, 3552 (1952).

[28] C. W. L. Bevan, *ibid.*, 2340 (1951).

[29] J. D. Reinheimer, R. C. Taylor, and P. E. Rohrbaugh, *J. Amer. Chem. Soc.*, **83**, 835 (1961).

[30] S. D. Ross, *ibid.*, **81**, 2113 (1959).

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.

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