**Nitrolysis.** The nitrolyses were carried out by three general methods. Properties and analytical data for new products are listed in Table I.

**Method A.** The dialkyl *tert*-butylamine was added to concentrated $H_2SO_4$ with cooling in ice. To this mixture was added at 0 °C a mixture of 90% $HNO_3$ and concentrated $H_2SO_4$. After being stirred, the solution was poured onto ice and the product isolated as described below.

**Method B.** The dialkyl *tert*-butylamine was added to 100% $HNO_3$ at 0 °C under $N_2$. After being stirred, the solution was poured onto ice and the product isolated as described below.

**Method C.** To acetic anhydride under $N_2$ was added 100% $HNO_3$, keeping the temperature below 20 °C. To this solution at 5–10 °C was added the dialkyl *tert*-butylamine in AcOH. After being stirred, the solution was poured onto ice and the product isolated as described below.

**1,3,3,5,5-Pentanitropiperidine (4).** Method A, with 0.2 g of 1 in 3 mL of $H_2SO_4$ and a mixture of 0.8 mL of $HNO_3$ and 1.3 mL of $H_2SO_4$ and after overnight stirring at room temperature, filtering off of the solid, washing with water, and recrystallization ($CH_2Cl_2$/hexane), gave 0.15 g (81%) of **4**. Method B, with 0.1 g of **1** and 2 mL of $HNO_3$ and after 3 days at room temperature, filtering off of the solid, extraction of the filtrate ($CH_2Cl_2$), and purification of the product as in method A, gave 0.09 g (96%) of **4**. The products were identical by melting point and IR with an authentic sample.

**1,3,5,5-Tetranitrohexahydro-1,3-diazine (6).** Method A, with 7.5 g of **5** in 100 mL of $H_2SO_4$ and a mixture of 17 mL of $HNO_3$ and 27 mL of $H_2SO_4$ and after 1 h at 0 °C and 2 h at room temperature, extraction ($CH_2Cl_2$), drying ($MgSO_4$), concentration, addition of hexane, and cooling, gave 6.05 g (87%) of **6**.

**3,5,5-Trinitrotetrahydro-1,3-oxazine (8).** Method C, with 2 mL of $Ac_2O$, 0.8 mL of $HNO_3$ and 1.0 g of **7** in 2 mL of AcOH and after warming of the mixture to room temperature over 4 h and overnight stirring at room temperature, extraction ($CH_2Cl_2$), washing with $H_2O$, and purification by recrystallization ($CH_2Cl_2$/hexane), gave 0.56 g (54%) of **8**.

**1,3,5,7-Tetranitro-3,7-diazabicyclo[3.3.1]nonane (10).** Method B, with 0.2 g of **2** and 2.0 mL of $HNO_3$ and after 0.5 h at 0 °C and 3 days at room temperature, filtering off of the solid, extraction of the filtrate ($CH_2Cl_2$), washing of the extract with dilute $K_2CO_3$ solution and $H_2O$, and recrystallization ($CH_2Cl_2$/hexane) of the combined product, gave 0.11 g (59%) of **10**.

**7-*tert*-Butyl-1,3,5-trinitro-3,7-diazabicyclo[3.3.1]nonane (9).** Method A, with 0.1 g of **2** in 2.5 mL of $H_2SO_4$ and a mixture of 0.6 mL of $HNO_3$ and 1 mL of $H_2SO_4$ and after 1 h at 0 °C and 1 h at room temperature, extraction ($CH_2Cl_2$), washing with dilute $K_2CO_3$ solution and $H_2O$, and recrystallization (MeOH/$H_2O$), gave 0.06 g (62%) of **9**.

**1-*tert*-Butyl-3,5-dinitro-5-methyl-1,3-hexahydrodiazine (13).** Method A, with 0.1 g of **3** in 2.5 mL of $H_2SO_4$ and a mixture of 0.6 mL of $HNO_3$ and 1.0 mL of $H_2SO_4$ and after 15 min at 0 °C, extraction ($CH_2Cl_2$), washing with $H_2O$, and recrystallization of the crude product (MeOH/$H_2O$), gave 0.07 g (77%) of **13**.

**5-Methyl-1,3,5-trinitrohexahydro-1,3-diazine (12).** Method B, with 5 mL of $HNO_3$ and 0.1 g of **3** and after 15 min at 0 °C and 6 h at 35–45 °C, filtering off the solid, and recrystallization ($CH_2Cl_2$/hexane), gave 0.043 g (51%) of **12**.

**Nitrolysis of *tert*-Butyldimethylamine.** To 10 mL of $Ac_2O$ at 0–5 °C was added 2.9 mL of oxide-free 90% $HNO_3$, followed by a solution of 1.0 g of *tert*-butyldimethylamine in 3.0 mL of AcOH. The mixture was stirred 2 days at room temperature and poured onto ice. After the mixture was stirred 2 h, the product was extracted ($CH_2Cl_2$). The aqueous phase was made basic ($Na_2CO_3$) and extracted again ($CH_2Cl_2$). The combined extracts were washed (dilute $NaHCO_3$), dried ($MgSO_4$), and concentrated by distillation. Addition of hexane and chilling gave 0.143 g (16%) of dimethylnitramine. Further concentration gave no additional product.

**Nitrolysis of *tert*-Butyldimethylamine Hydrochloride.** The same procedure as above was used with 11.5 mL of $Ac_2O$, 2.5 mL of oxide-free $HNO_3$, and a solution of 2.0 g of the amine hydrochloride in 2 mL of AcOH. A workup as above gave 0.51 g of dimethylnitramine as a first crop. Further concentration gave another 0.21 g (total yield 55%).

**Acknowledgment.** This work was supported by the Energetic Materials Division, U.S. ARRADCOM, Dover, NJ, and the Office of Naval Research, Mechanics Division, Code 432.

**Registry No.** **1**, 81340-11-6; **2**, 81340-12-7; **3**, 65478-96-8; **4**, 71706-07-5; **5**, 34924-01-1; **6**, 81360-42-1; **7**, 33923-30-7; **8**, 81340-13-8; **9**, 81340-14-9; **10**, 81340-15-0; **12**, 81340-16-1; **13**, 81340-17-2; *tert*-butylamine, 75-64-9; 2,2-dinitro-1,3-propanediol, 2736-80-3; nitromethane, 75-52-5; nitro ethane, 79-24-3; *tert*-butyldimethylamine, 918-02-5; dimethylnitramine, 4164-28-7; *tert*-butyldimethylamine hydrochloride, 6338-78-9.

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## Competing β Fragmentation in Regeneration of Alcohols from Arenesulfonates with Arene Anion Radicals

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The recovery of alcohols from alkyl arenesulfonates through reductive cleavage with arene anion radicals has found considerable use,[1] since the process usually proceeds in excellent yield with few side reactions such as elimination, racemization, or epimerization.[2] Recently, Cavazza et al. reported that benzylic and allylic tosylates undergo considerable C–O cleavage on treatment with sodium–naphthalene or sodium–anthracene.[3] Yields of alcohol were sometimes as low as 30%, and sizeable amounts of products characteristic of further reaction of allylic or benzylic radicals or anions were also found.[3] We report that certain other types of arenesulfonate esters are prone to a different side reaction which yields products characteristic of carbon radicals produced by cleavage of the C–C bond β to the O–S bond of the sulfonate ester.

For example, neopentyl tosylate (**1**) on treatment with sodium–naphthalene in tetrahydrofuran (THF) yields both neopentyl alcohol and a mixture of what appears to be 1- and 2-*tert*-butyldihydronaphthalene. Traces of isobutane could also be observed in most reaction mixtures. Under similar conditions the *p*-toluenesulfonate ester of 2-methyl-2-phenylpropanol (neophyl tosylate, **2**) affords a sizeable amount of cumene as well as neophyl alcohol and traces of what appear to be alkylated dihydronaphthalenes. Typical results are shown in Table I.

In our original studies neopentyl tosylate was observed to give an anomalously low yield of alcohol (ca. 85%) even under quite favorable conditions (large excess of sodium naphthalene, 0 °C).[2] Further work showed that the yield of alcohol was even poorer under the conditions used in this study (slight excess of anion radical, 25 °C) and that changing the solvent from THF to 1,2-dimethoxyethane (DME) resulted in a further drop in yield. In addition, small amounts of two long-retention-time materials were observed on gas chromatographic (GC) analysis. The

(1) H. C. Jarrell, R. G. S. Ritchie, W. A. Szarek, and J. K. N. Jones, *Can J. Chem.*, **51**, 1767 (1973); L. A. Paquette, R. W. Beglund, and P. C. Storm, *J. Am. Chem. Soc.*, **92**, 1971 (1970); L. A. Paquette and P. C. Storm, *ibid.*, **92**, 4295 (1970); H. L. Goering and R. W. Thies, *ibid.*, **91**, 2967 (1969); S. A. Roman and W. D. Closson, *ibid.*, **91**, 1701 (1969); R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969); W. D. Closson and G. T. Kwiatkowski, *ibid.*, 6436 (1966).

(2) W. D. Closson, P. Wriede, and S. Bank, *J. Am. Chem. Soc.*, **88**, 1581 (1966).

(3) M. Cavazza, F. Del Cima, L. Nucci, L. Fabiani, and F. Pietra, *J. Org. Chem.*, **44**, 4999 (1979).

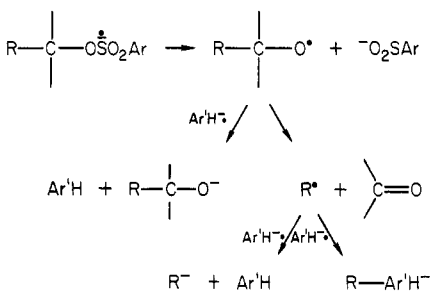
0022-3263/82/1947-2476$01.25/0 

Table I. Reaction of Arenesulfonate Esters with Arene Anion Radicals

| sulfonate ester | anion radical[b] | solvent | % yield of products[a] ArH | ROH | RH[c] | other |
|---|---|---|---|---|---|---|
| neopentyl *p*-toluenesulfonate (1a) | naphthalene | THF | 59 | 70 | trace | 4.6[d] |
| 1a | naphthalene | DME | 50 | 39 | trace | 21[d] |
| neopentyl *p*-fluorobenzenesulfonate (1b) | naphthalene | DME | | 34 | trace | 21[d] |
| neopentyl *p*-methoxybenzenesulfonate (1c) | naphthalene | DME | | 46 | trace | 20[d] |
| neophyl *p*-toluenesulfonate (2) | naphthalene | THF | 39 | 50 | 13 | *e* |
| 2 | naphthalene | DME | 58 | 54 | 13 | *e* |
| 2 | anthracene | DME | 8.5 | 30 | 7 | |
| 2 | acenaphthylene | DME | 20 | 20 | 5 | |
| 2,2-dimethylhexyl *p*-toluenesulfonate (3) | naphthalene | DME | 83 | 41 | trace | *e* |
| 3,3-dimethyl-2-butyl *p*-toluenesulfonate (4) | naphthalene | THF | | 96 | | |
| 4 | naphthalene | TG | | 47 | | *e* |
| 2-phenethyl *p*-toluenesulfonate (5a) | naphthalene | THF | | 99[f] | | |
| 2-phenethyl benzenesulfonate (5b) | naphthalene | DME | | 93 | <0.5 | |
| *endo*-5-norbornon-2-yl *p*-toluenesulfonate (8) | anthracene | THF | | 43[g] | | |
| 8 | anthracene | THF[h] | | 72[h,i] | | |
| 8 | naphthalene | DME | | 50[j] | | *k* |

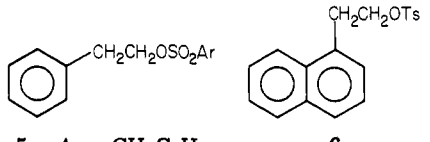
[a] Based on the amount of sulfonate ester. [b] Sodium salt. [c] Alkane of one less methyl group. [d] Mixture of *tert*-butyldihydronaphthalenes (see text). [e] Alkylated dihydronaphthalenes detected but not measured. [f] Data from ref 2. [g] Consists of 23% endo and 20% exo alcohol. [h] Reaction carried out at −60 °C. [i] Consists of 58% endo and 14% exo alcohol. [j] Approximately 25% each of endo and exo alcohols. [k] Traces of other alcohols (see text).

Scheme I




pattern and retention time of these slightly overlapping peaks were identical with those produced on treatment of sodium–naphthalene solutions with *tert*-butyl chloride. Isolation of the peaks from the reaction with **1a** and treatment with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) produced two new compounds, one of which proved to be identical with authentic 2-*tert*-butylnaphthalene. The other component, of slightly shorter retention time, is almost certainly the other positional isomer. Treatment of a solution of sodium–naphthalene in DME with either neopentyl chloride or neopentyl methanesulfonate, reactions that should produce some neopentyldihydronaphthalenes,[4,5] yielded material with definitely longer retention times. Isobutane could usually be detected among the products from neopentyl arenesulfonates, but the amount was quite low and rather variable.

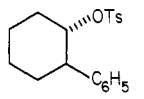
The formation of *tert*-butyldihydronaphthalenes, and probably of isobutane, in these reactions strongly implies the intermediacy of *tert*-butyl radical.[4] The most likely source of such radicals would be β fragmentation of a neopentyloxy radical.[6] The simplest mechanism would be that shown in Scheme I. Initial cleavage of the ester anion radical could proceed in the sense shown, yielding alkoxy radical and sulfinate anion. The alkoxy radical could then either be reduced further to alkoxide or fragment to alkyl radical and carbonyl fragment. Further reaction of the alkyl radical with arene anion radical would be expected to yield the observed alkylated dihydroarene and alkane.[4] From this simple scheme one would expect that sulfonate esters most prone to yield fragmentation products would be those where the ejected alkyl radical would be relatively stable, i.e., tertiary, benzylic, or allylic. Neophyl tosylate (**2**), where the alkyl radical would be the exceptionally stable cumyl structure, and the tosylates of 2,2-dimethylhexanol (**3**) and 3,3-dimethyl-2-butanol (**4**), which would yield tertiary alkyl radicals, seem to be particularly prone to β fragmentation. Sulfonate esters which would yield primary or secondary benzylic radicals seem to be more resistant to such fragmentation since 2-phenylethyl (**5a**), 2-(1-naphthyl)ethyl (**6**), and *trans* 2-



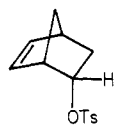

**5a**, Ar = $CH_3C_6H_4$
b, Ar = $C_6H_5$




**6**




**7**



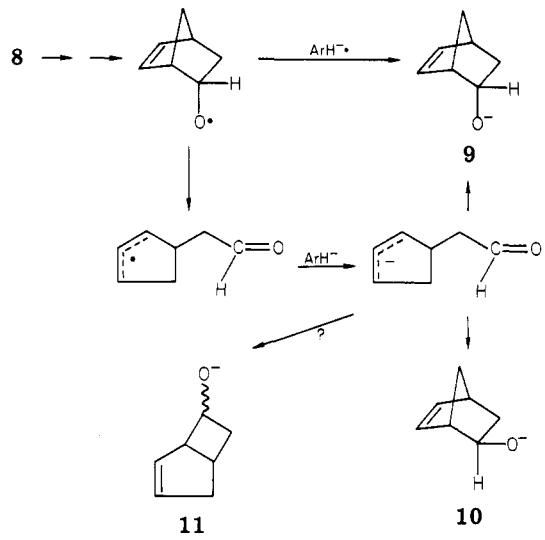

**8**

phenylcyclohexyl tosylate (**7**) all gave good yields of the parent alcohols in our original study.[2] Interestingly, though, a careful examination of the product mixture from reaction of 2-phenylethyl benzenesulfonate (**5b**) with sodium–naphthalene in DME does reveal formation of a very small amount of toluene, the expected major product from formation of benzyl radical under these conditions (see Table I).

As for systems which might generate an allylic radical, the only one we have examined is *endo*-5-norbornen-2-yl tosylate (**8**). This, on treatment with arene anion radicals, yields both *exo*- (**9**) and *endo*-5-norbornen-2-ol (**10**). Since the alcohols themselves could be shown not to be epimerized under the conditions of the reactions, we propose the mechanism shown in Scheme II to account for formation of the exo isomer. Two additional minor peaks, slightly after those corresponding to **9** and **10**, were also observed on GC analysis of the reaction mixture from sodium–naphthalene. Though quantities were too small to permit thorough identification, we suggest that they are probably the [3.2.0] isomers represented by **11**. Though

(4) J. F. Garst, *Acc. Chem. Res.*, **4**, 400 (1971).
(5) J. R. Ganson, S. Schulenberg, and W. D. Closson, *Tetrahedron Lett.*, 4397 (1970).
(6) W. A. Pyror, "Free Radicals", McGraw-Hill, New York, 1966, pp 84–87; P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

Scheme II




Scheme II shows recyclization proceeding via reduction of the ring-opened radical to allylic carbanion, the initial step might involve reduction of the carbonyl group to ketyl anion radical, followed by coupling in a fashion similar to the observed reaction between diaryl ketyls and alkyl radicals.[7]

Other factors that might affect the extent of $\beta$ cleavage were briefly examined. Minor changes in the arenesulfonate portion did not appear to have much effect: the *p*-fluorobenzenesulfonate (**1b**) and *p*-methoxybenzenesulfonate of neopentyl alcohol (**1c**) gave essentially the same mixtures of products as did the tosylate when treated with sodium–naphthalene in DME. The effect of changing the electron donor was tested by using neophyl tosylate. The poorer reducing agents sodium–anthracene and sodium–acenaphthalene gave diminished yields of both alcohol and of cumene. Interpretation of these results is hampered by the poor material balance. The effect of solvent change is striking in some instances. Changing from THF to DME or tetraglyme (TG) results in a decrease in alcohol yield and an increase in yield of fragmentation products in several cases. These changes in solvent would result in changing the state of sodium–naphthalene from tight ion pairs in THF to loose or "glymated" species in DME or TG.[8] The latter species have been shown often to be much more potent reducing agents.[9] The increase in fragmentation observed in certain cases runs counter to what might be expected from Scheme I. A stronger reducing agent should *increase* the rate of direct reduction of alkoxy radical at the expense of $\beta$ fragmentation. On the other hand, concentration and temperature effects noted in a few cases seem to support the simple competition shown in Scheme I. For example, the yield of alcohol from neopentyl tosylate is about 85% when it is added to ca. 0.5 M sodium–naphthalene (THF)[2] but is only 70% when anion radical solution is slowly added to a solution of the ester (this study). The norbornenyl ester 8 yields more unrearranged and less rearranged alcohol on reaction with sodium–anthracene on lowering of the temperature to −60 °C.

The actual mechanism is probably more complex than that shown in Scheme I. The partitioning of alkyl radical between alkane and alkylation products normally produces 35–60% alkane as shown from reactions of alkyl halides with sodium–naphthalene.[4,10] (Benzylic radicals are reduced almost entirely to carbanions under these conditions).[11] In the sulfonate fragmentation reactions, the yields of alkanes are often vanishingly small. An explanation for this may be that reduction of alkyl radical (which is felt to occur at the diffusion-controlled rate)[4] takes place in such proximity to the ejected carbonyl fragment that regeneration of alkoxide is a major reaction pathway. (As noted earlier, reduction of the carbonyl compound to a ketyl could also lead back to alkoxide.) This could mean that a good deal of "masked" fragmentation is occurring in these reactions and that product composition may be affected by factors other than the competition between reduction and fragmentation of the alkoxy radicals.

The results do imply that the normal mechanism of reaction of arenesulfonate esters involves (at least in part) one-electron cleavage of the S–O bond, producing alkoxy radical and arenesulfinate anion. The C–O cleavage observed by Cavazza and co-workers[3] is apparently limited to those cases where the alkyl group is a particularly stable radical itself (e.g., those derivable from allylic, benzylic, and, possibly, tertiary arenesulfonates).

Table II. Melting Points of Arenesulfonate Esters

| sulfonate ester | mp, °C | lit. mp, °C |
|---|---|---|
| 1a | 45.5–46.5 | 47–48[a] |
| 1b | 48–49 | *b* |
| 1c | 33–35 | *b* |
| 2 | 74.5–75.1 | 74–75[c] |
| 3 | 25–27 | *b* |
| 4 | liquid[d] | |
| 5a | 37.5–38.5 | 37.2–38.2[e] |
| 5b | 13 | *b* |
| 8 | 62.5–63.5 | 63.5–64.5[f] |

[a] U. K. Pandit and M. C. Kloetzel, *J. Am. Chem. Soc.*, **83** 83, 482 (1961). [b] Satisfactory analytical data were reported for these new compounds. [c] S. Winstein, B. K. Morse, E. G. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952). [d] Refractive index $n^{20}_D$ 1.5008; lit. $n^{20}_D$ 1.5007 [A. H. Fainberg and S. Winstein, *J. Am Chem. Soc.*, 78, 2780 (1956)]. [e] W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **80**, 2421 (1958). [f] S. Winstein and M. Shatavsky, *ibid.*, 78, 592 (1956).

## Experimental Section

**Materials and Equipment.** Solvents (tetrahydrofuran, 1,2-dimethoxyethane, tetraglyme) were distilled from either lithium aluminum hydride or sodium benzophenone ketyl and stored under nitrogen. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 instrument equipped with flame-ionization detectors and 6 ft × 0.125 in., 10% silicone rubber (UC-W98) or 10% Carbowax 20M on Chromosorb W columns. Yields by GC were determined by using internal standards and measuring peak areas by cutting and weighing. NMR spectra were recorded by using a Varian A-60A instrument.

**Arenesulfonate esters** were prepared by treating the appropriate alcohol with arenesulfonyl chloride in pyridine after the general method of Tipson.[12] Their physical properties are described in Table II.

**Arene anion radical solutions** were prepared and handled as described previously.[13]

(7) J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.*, **95**, 6870 (1973).
(8) M. Szwarc and J. Jagur-Grodzinski, "Ions and Ion Pairs in Organic Reactions", Vol. 2, Wiley-Interscience, New York, 1974, Chapter 1.
(9) S. Bank and D. A. Juckett, *J. Am. Chem. Soc.*, **97**, 567 (1975).
(10) G. D. Sargent and G. A. Lux, *J. Am. Chem. Soc.* **90**, 7160 (1968).
(11) Y. J. Lee and W. D. Closson, *Tetrahedron Lett.*, 1395 (1974).
(12) R. S. Tipson, M. A. Clapp, and L. H. Cretcher, *J. Org. Chem.*, 12, 133 (1947).
(13) W. D. Closson, S. Ji, and S. Schulenberg, *J. Am. Chem. Soc.*, **92**, 650 (1970).

Table III. Analytical Data for New Compounds

| | |
|---|---|
| 1b | high-resolution mass spectrum,[a] $m/z$ 246.0720 ($C_{11}H_{15}FO_3S$ requires 246.0726) |
| 1c | anal.[b] calcd for $C_{12}H_{17}O_4S$: C, 55.82; H, 7.02. Found: C, 56.03; H, 6.98 |
| 3 | high-resolution mass spectrum,[a] $m/z$ 284.1441 ($C_{15}H_{24}O_3S$ requires 284.1446) |
| 5b | solvolysis equivalent,[c] 269 ± 2 ($C_{14}H_{18}O_3S$ requires 266.1) |

[a] By Dr. Woodfin Ligon, General Electric Research and Development Center, Schenectady, NY. [b] Instranal Laboratory, Inc., Rensselaer, NY. [c] Weighed samples were heated with measured amounts of sodium acetate in acetic acid and then back-titrated with standard perchloric acid in acetic acid solution.

**2-*tert*-Butylnaphthalene** was prepared after the manner of Crawford and Glesmann[14] and purified by preparative GC: NMR ($CDCl_3$) $\delta$ 1.4 (s, 9 H), 7.2–7.8 (m, 7 H).

**Reaction of Sulfonate Esters with Arene Anion Radicals.** The general procedure was to place measured quantities of sulfonate ester (0.1–0.2 mmol) and internal standard (usually an alkane of suitable molecular weight) in a 10-mL vial equipped with glass covered stirring bar and septum cap. To this was added ca. 5 mL of dry solvent, and the system was thoroughly flushed with dry $N_2$ or Ar. Anion radical solution (0.2–0.4 M) was then added dropwise via syringe until the intense color of the reagent persisted. The contents of the vial were stirred and cooled (if noted in Table I) during this period. After being stirred for an additional 10 min, the reaction mixture was treated with a few drops of water and dried with a small amount of magnesium sulfate. Analysis by GC was then carried out directly on this solution. Various data for the new compounds are given in Table III.

**Acknowledgment.** This research was supported in part by Grant No. 77-3241A from the Air Force Office of Scientific Research. We thank Dr. Ann Ligon for experimental assistance and consultation.

**Registry No.** 1a, 2346-07-8; 1b, 81390-32-1; 1c, 81390-33-2; 2, 21816-03-5; 3, 60697-64-5; 4, 25966-61-4; 5a, 4455-09-8; 5b, 32376-95-7; 8, 5906-87-6; naphthalene radical ion (1–) sodium salt, 3481-12-7; anthracene radical ion (1–) sodium salt, 12261-48-2; acenaphthylene radical ion (1–) sodium salt, 81390-34-3; neopentyl alcohol, 75-84-3; $\beta,\beta$-dimethylbenzenethanol, 2173-69-5; 2,2-dimethylhexanol, 2370-13-0; 3,3-dimethyl-2-butanol, 464-07-3; benzenemethanol, 100-51-6; *endo*-bicyclo[2.2.1]hept-5-en-2-ol, 694-97-3; *exo*-bicyclo[2.2.1]hept-5-en-2-ol, 2890-98-4; 1-*tert*-butyldihydronaphthalene, 81390-35-4; 2-*tert*-butyldihydronaphthalene, 81390-36-5; cumene, 98-82-8; naphthalene, 91-20-3; anthracene, 120-12-7; acenaphthylene, 208-96-8.

(14) H. M. Crawford and M. C. Glesmann, *J. Am. Chem. Soc.* **76**, 1108 (1954).

## Synthesis of $\alpha$-Phenylthio Aldehydes and Alkylation of 2-(Phenylthio)octanal Enolate

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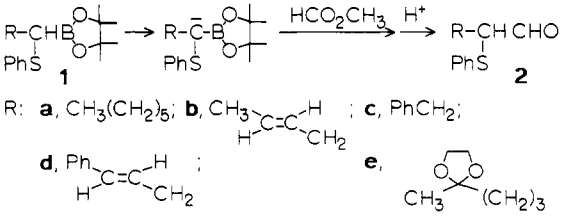
The preparation and $\alpha$-lithiation of $\alpha$-(phenylthio)alkaneboronic esters (1) and their condensation with carboxylic esters to provide a regiospecific synthesis of $\alpha$-phenylthio ketones has been reported.[1] We have now extended this chemistry to formate esters and have found

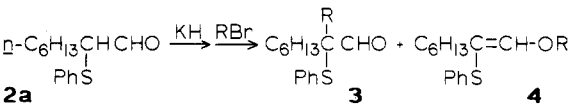



that $\alpha$-phenylthio aldehydes (2) are readily prepared in good yields, as summarized in Table I. To demonstrate the potential utility of 2 as synthetic intermediates, we have studied the $\alpha$-deprotonation of $\alpha$-(phenylthio)octanal (2a) and the alkylation of the resulting enolate by allyl and other reactive halides, as summarized in Table II.

$\alpha$-Phenylthio aldehydes have been made previously from aldehyde enolates by Seebach and Teschner,[2] and reactions of $\alpha$-thio aldehydes have been described by Duhamel and co-workers.[3]

Two reports of direct alkylation of aldehydes have appeared. Isobutyraldehyde has been C alkylated with benzyl chloride in the presence of sodium hydroxide and a phase-transfer catalyst.[4] A more general reaction is the generation of aldehyde enolates with potassium hydride in tetrahydrofuran (THF) and their alkylation with allylic or benzyl halides.[5] The latter approach proved applicable to an $\alpha$-phenylthio aldehyde.

Addition of 2-(phenylthio)octanal (2a) to a suspension




R: 3 and 4 a, $CH_2$=$CHCH_2$-; b, E-$CH_3CH$=$CHCH_2$-; c, $(CH_3)_2C$=$CHCH_2$-; d, $PhCH_2$-; e, $CH_3$-

of potassium hydride in THF at room temperature resulted in hydrogen evolution and formation of the enolate within a few minutes. It was verified that conversion to enolate is complete by quenching a sample with $D_2O$, which led to recovered octanal that lacked any measurable absorption by the $\alpha$ proton at $\delta$ 3.4 and had a singlet in place of the usual CHO doublet at $\delta$ 9.2. Addition of allyl bromide or a similarly reactive halide led to a mixture of C alkylation and O alkylation products 3 and 4, respectively, as summarized in Table II. When a mixture of cyclohexane and benzene was used in place of THF as solvent, formation of the enolate was slower but the proportion of C alkylation product (3) became much more favorable (Table II). In contrast, addition of an equivalent of dicyclohexyl-18-crown-6 resulted in exclusive O alkylation of 2a to 4c by phenyl bromide in THF.

In contrast to the highly successful results with allylic halides, a single attempted reaction of the potassium enolate of 2a with a typical primary halide, *n*-propyl iodide, yielded no alkylation product whatever, as indicated by TLC and NMR analysis of the reaction mixture. Although primary alkyl iodides have been reported to alkylate simple aldehyde enolates,[5] they gave lower yields and more O alkylation than allylic bromides, and this precedent did not encourage us to pursue the matter further.

### Experimental Section

Reactions involving carbanions were run under argon in oven-dried glassware, with transfer of reagents by syringe.

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