

REACTIONS OF AROMATIC RADICAL ANIONS. X. SYNTHESSES USING A CONVENIENTLY RECOVERABLE
RADICAL ANION PRECURSOR

Shelton Bank and Matthew Platz

Department of Chemistry
State University of New York at Albany
Albany, New York 12222

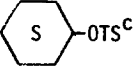
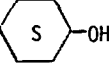
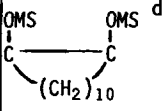
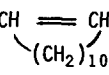
(Received in USA 19 March 1973; received in UK for publication 27 April 1973)

In the past few years the high selectivity and yields of radical anion syntheses have found value for the cleavage of tosylates^{1a} and sulfonamides^{1b}, preparation of alcohols^{1c}, amines^{1d}, anions^{1e}, olefins^{1f,g}, strained cyclic compounds^{1h}, Grignard reagents¹ⁱ, organo-metallic reagents^{1j} and activated sodium hydride^{1k}. Product isolation involves separation from the radical anion precursor (e.g. naphthalene) and is often difficult.² It is desirable to have an alternative radical anion precursor that reacts similarly to sodium naphthalene but can be simply and completely removed by extraction. We are pleased to report that α -dimethylaminonaphthalene (DIMAN) fulfills these conditions.

Preparation of solutions of sodium DIMAN is as straightforward as of sodium naphthalene. Thus stirring freshly cut sodium, DIMAN and solvent, tetrahydrofuran (THF) or dimethoxyethane (DME), in a dry, oxygen-free vessel results in the formation of a dark green color in minutes and reaction is complete in several hours. Solutions as concentrated as 1 M. have been made with no difficulty. For our comparative study, four characteristic and diverse sodium naphthalene reactions were investigated: cleavage of cyclohexyl tosylate to cyclohexanol, elimination in 1,2 cyclododecane dimesylate to cyclododecene, preparation of benzyltrimethylsilane from benzyl chloride and trimethyl silylchloride and reaction with hydrogen to give activated sodium hydride.³ In each instance DIMAN was quantitatively removed by successive washings with aqueous acid. Table 1 records the pertinent data. Yields with sodium DIMAN are comparable to those with sodium naphthalene, although somewhat lower. More significantly, the isolated yields of pure products are substantial and should render the reagent of synthetic use.

Preliminary experiments indicate that the chemistry of sodium DIMAN is similar to that of

TABLE I
Product Yields with Sodium DIMAN

Reactant	Product	Yield ^a % () ^b	NaNaph ^a Yield %	Ref
		64 (55)	98	1a
		84 (67)	98	1g
H ₂	NaH	98 ^e	100 ^e	1k
φ-CH ₂ Cl + Me ₃ SiCl ^f	φ-CH ₂ SiMe ₃	63 (55)	95	1j

- Determined by glc using internal standards.
- Isolated as the pure compound after vacuum distillation.
- The tosylate is added to a four fold excess of sodium DIMAN at room temperature. The excess radical anion is quenched by bubbling O₂ into the solution.
- The dimesylate, sodium and DIMAN are added to DME at room temperature until the green color persists.
- Titanium tetraisopropoxide used as a catalyst and yield is determined by H₂ evolution upon addition of acetone.
- A 2:1 mixture of benzylchloride and trimethyl silylchloride is added rapidly to sodium DIMAN at -70°.

sodium naphthalene. Reaction with oxygen results in quantitative recovery of DIMAN and reaction with water leads to recovery of 50% of the DIMAN and an equal amount of a dihydro

derivative of DIMAN.⁴ We found no evidence for cleavage of the dimethylamino group. Sodium DIMAN reacts slowly with THF, however to give both cis and trans crotyl alcohol and for this reason synthetic reactions are run preferentially in DME as solvent decomposition products, if any, do not interfere with product isolation.

The rapid and extensive formation of sodium DIMAN radical anion indicates that the conjugative effect of the dimethylamino group does not significantly raise the reduction potential of the naphthalene ring. Quite possibly the operative effect is an internal solvation of the sodium ion, similar to that observed for various other organometallic compounds.⁵ We are presently undertaking experiments to determine the solvation sphere size and to prepare the dianion of this naphthalene ring system.

Acknowledgment: We are grateful to the National Science Foundation for support of this work.

References

1. a. W. D. Closson, P. Wriede and S. Bank, J. Amer. Chem. Soc., 88, 1581 (1966).
- b. S. Ji, L. B. Gortler, A. Waring, A. Battisti, S. Bank, W. D. Closson and P. Wriede, J. Amer. Chem. Soc., 89, 5311 (1967); S. Ji, S. Schulenberg and W. D. Closson, J. Amer. Chem. Soc., 92, 650 (1970).
- c. E. J. Corey, J. Amer. Chem. Soc., 92, 395 (1970).
- d. J. Jacobus, M. Raban and K. Mislow, J. Org. Chem., 33, 1142 (1968).
- e. J. J. Eisch, J. Org. Chem., 28, 707 (1963); H. S. Mosher, J. Org. Chem., 32, 2797 (1967).
- f. C. G. Scouten, F. E. Barton, Jr., J. R. Burgess, Jr., P. R. Story and J. F. Garst, Chem. Comm., 1969, 78; J. S. McKennis, L. Brenner, J. R. Schweiger and R. Pettit, Chem. Comm., 1972, 365.
- g. J. C. Carnahan and W. D. Closson, Tetrahedron Letters, 3447 (1972).
- h. H. W. Whitlock, Jr. and P. F. Schatz, J. Amer. Chem. Soc., 93, 3837 (1971).
- i. S. Bank and J. F. Bank, Tetrahedron Letters, 4533 (1969).
- j. S. Bank and J. F. Bank, Tetrahedron Letters, 4581 (1971).
- k. S. Bank and T. A. Lois, J. Amer. Chem. Soc., 90, 4505 (1968).

2. D. B. Ledlie, R. L. Thorne and G. Weiss, J. Org. Chem., 35, 2186 (1971).
3. A representative procedure is as follows: 7.30g Sodium (0.32mole), 51.0g DIMAN (0.30 moles), and 240 ml of dry THF are stirred under a nitrogen atmosphere for two hours. The dark green solution is cooled to -70° with a Dry Ice-acetone mixture. Mechanical stirring is necessary to agitate the cold viscous solution. A mixture of 7.80g (0.060moles) benzyl chloride and 21.0g (0.120moles) of trimethylsilyl chloride is added rapidly. The reaction mixture is allowed to come to room temperature, at which point it is filtered and washed twice with 40 ml portions of concentrated hydrochloric acid. The organic phase is dried over $MgSO_4$ and the solvent is carefully removed. The product trimethyl benzylsilane is vacuum distilled (94-96^o/33 mm, 5.6g, 0.033moles) in 55% yield.

DIMAN can be recovered by carefully raising the pH of the acid wash with sodium hydroxide to 14, and then ether extraction (three times with 100ml portions). After drying with $MgSO_4$ and removing the solvent, 51.0g of DIMAN (100% recovery) remains. the DIMAN can be further purified by vacuum distillation (132-134^o/9mm) over CaH_2 .

4. The nmr analysis clearly shows that the product is a dihydro DIMAN derivative although we have no information on which isomer(s) are present.
5. H. G. Richey, W. F. Erickson and A. S. Heyn, Tetrahedron Letters, 2183, 2187 (1971) and references cited therein.