References and Notes

(1) E. Buncel, A. R. Norris, and K. E. Russell, *Q. Rev. Chem. Soc.*, **22**, 123 (1968).
(2) P. Buck, *Angew. Chem., Int. Ed. Engl.*, **8**, 120 (1969).
(3) M. R. Crampton, *Adv. Phys. Org. Chem.*, **7**, 211 (1969).
(4) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).
(5) C. F. Bernasconi, *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, **3**, 33 (1973).
(6) T. N. Hall and C. F. Poranski, Jr., in "The Chemistry of the Nitro and Nitroso Groups", Part 2, H. Feuer, Ed., Interscience, New York, N.Y., 1970, p 329.
(7) R. R. Bard, Ph.D. Thesis, University of Vermont, 1977.
(8) R. R. Bard and M. J. Strauss, *J. Org. Chem.*, **41**, 2421 (1976).
(9) M. J. Strauss, T. C. Jensen, H. Schran, and K. O'Connor, *J. Org. Chem.*, **35**, 383 (1970).
(10) R. J. Pollitt and B. C. Saunders, *J. Chem. Soc.*, 4615–4628 (1965).
(11) The authors thank the editor for pointing this out.
(12) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(13) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, N.Y., 1972.
(14) The authors thank Dr. David Palmer (Princeton University) for obtaining this spectrum. It was run in Me_2SO-d_6 with Me_4Si as an internal standard.

A Convenient Preparation of Deuterated Aromatic Compounds

John W. Larsen* and Laurence W. Chang

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916, and Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Received March 3, 1978

The classical procedures for the deuteration of polycyclic aromatics are tortuous and inconvenient,[1] involving heating the arene in D_2O to 350 °C in the presence of a Pt catalyst or exchange with benzene-d_6.[2] A more convenient procedure for the deuteration of benzo[*a*]pyrene was recently published.[3] There also exists an excellent method developed by Makabe, but since it was published in Japanese it has not been used widely in the west.[4] Their elegant method uses a mixture of $BF_3{\cdot}D_3PO_4$ and is useful with a variety of organic compounds. This experimental procedure was improved by Heredy and co-workers.[5] The use of liquid deuteriohalides has also been reported.[6] We have developed another technique for preparing deuterated aromatic compounds which is very rapid and convenient, requiring only BF_3 and D_2O.

The liquid acid prepared by blowing BF_3 gas into D_2O to prepare a 1:1 molar solution is a fascinating, strong acid system[7,8] whose chemistry we are exploring. Its preparation is rapid and easy. It can be used for preparing deuterated aromatics simply by stirring the neat aromatic with the $BF_3{\cdot}D_2O$ system. Reactions with deactivated benzenes are too slow to be useful. The reaction proceeds nicely with polycyclic aromatics and others whose electrophilic reactivity is as great as or greater than benzene. The system has obvious advantages over D_2SO_4. Since the proton is the only electrophile, competing electrophilic reactions such as sulfonation do not occur. Since BF_3 and D_2O are commonly available, the procedure is much more convenient than the use of deuteriohalides such as DBr and $AlBr_3$ or DF or DCl in CF_3COOD.[6] Results with a variety of aromatics are given in Table I.

Experimental Section

All compounds were purchased and were used without further purification.

Preparation of $BF_3{\cdot}D_2O$. A weighed amount of D_2O (99.8%) was cooled in a ice–water bath and BF_3 was bubbled into the liquid until a 1:1 molar ratio was reached as measured by the weight increase. $BF_3{\cdot}D_2O$ is a fuming liquid and was stored in a polyethylene bottle.

Table I. Deuteration of Aromatic Compounds

compd	registry no.	temp, °C	time, h	H–D exchange, %
benzene	71-43-2	25	61	45
toluene	108-88-3	25	24	74
chlorobenzene	108-90-7	25	120	14
o-xylene	95-47-6	25	48	81
m-xylene	108-38-3	25	48	85
p-xylene	106-42-3	25	48	81
cumene	98-82-8	25	41	78
tert-butylbenzene	98-06-6	25	30	dealkylates
n-butylbenzene	104-51-8	25	48	70
tetralin	119-64-2	25	61	78
naphthalene	91-20-3	90	23	76
phenanthrene	85-01-8	105	20	81

Deuterium Exchange. The hydrocarbon was placed in a flask and a ca. 10 M excess of $D_2O{\cdot}BF_3$ was added. A condenser was connected and the reaction mixture was stirred at room temperature. Naphthalene and phenanthrene exchanges were carried out at 90 and 105 °C, respectively, in fuming, slowly decomposing acid. After completion, the organic layer was separated, washed twice with water, and dried with silica gel. Naphthalene and phenanthrene were dissolved in CCl_4 after the reaction, the CCl_4 layer was separated, washed with water, and dried over silica gel, and the CCl_4 was evaporated.

Analysis of Deuterium Exchange. The possibility of deuterium incorporation into the aliphatic groups was examined by looking for aliphatic C–D stretching bands in the IR spectrum. While a diminution of the C_{ar}–H stretch at about 3030 cm^{-1} and a new intense band at 2260 cm^{-1} due to C_{ar}–D stretch was observed, no bands attributable to C_{al}–D stretch were observed. Mass spectra indicated that a mixture of deuterated compounds was present in each reaction product. The extent of deuterium incorporation was measured by comparing the areas of the aromatic and aliphatic NMR peaks in the deuterated products. With benzene, chlorobenzene, naphthalene, and phenanthrene, D incorporation was estimated by adding a known amount of a standard compound (cyclohexane) to the CCl_4 solution of deuterated product and comparing peak areas. Reproducibility of the NMR technique was ±5% of the measured conversion.

Aknowledgment. Research sponsored by the Division of Basic Energy Sciences of the Department of Energy under contract with Union Carbide Corp. The helpful comments of Vernon Raaen and L. Maya are gratefully acknowledged.

Registry No.—D_2O, 7789-20-0; BF_3, 7637-07-2; $BF_3{\cdot}D_2O$, 33598-66-2.

References and Notes

(1) B. Chenon, L. C. Leitch, R. N. Renaud, and L. Tichat, *Bull. Soc. Chim. Fr.*, 38 (1964).
(2) M. A. Long, J. L. Garnett, and R. F. W. Vining, *J. Chem. Soc., Perkin Trans 2*, 1298 (1975).
(3) J. C. Seibles, D. M. Bollinger, and M. Orchin, *Angew. Chem., Int. Ed. Engl.*, **16**, 656 (1977).
(4) H. Makabe, S. Yokoyama, M. Itoh, and G. Takeya, *Hokkaido Daigaku Kogakubu Kenkyu Hokoku*, **62**, 77 (1971).
(5) R. P. Skowronski, J. J. Ratto, and L. A. Heredy, Quarterly Report for ERDA Contract E(49-18)-2328, Jan. 1977, Document No. FE-2328-7.
(6) A. I. Shatenshtein, "Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds", C. N. Turton and T. I. Turton translators, Consultants Bureau, New York, N.Y., 1962.
(7) L. Maya, *J. Inorg. Nucl. Chem.*, **39**, 225 (1977).
(8) D. W. A. Sharp in "Advances in Fluorine Chemistry", Vol. 1, M. Stacey, J. C. Talow, and A. G. Sharpe, Ed., Butterworths, London, 1960.

An Improved General Synthesis of 1-Aryl-1-cyclopropanols

Herbert C. Brown* and C. Gundu Rao[1]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

Received March 8, 1978

The most general procedure for the synthesis of 1-aryl-1-cyclopropanol previously available was that of De Puy and his co-workers[2] (eq 1). An alternative procedure, based on 1-

---

* Address correspondence to this author at Oak Ridge National Laboratory.

0022-3263/78/1943-3602$01.00/0