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CLEAVAGE OF TERT-BUTYLDIMETHYLSILYL ETHERS BY TETRAFLUOROBORATE SALTS

Brian W. Metcalf, Joseph P. Burkhart and Karin Jund
Department of Organic Chemistry
Merrell Research Center; Merrell-National Laboratories
2110 E. Galbraith Rd., Cincinnati, Ohio 45215

SUMMARY: Primary and secondary alcohols can be regenerated from their corresponding *tert*-butyl silyl ethers by treatment with tetrafluoroborate salts.

It has recently been reported that trimethylsilyl ethers of secondary alcohols, on treatment with triphenylcarbenium (trityl) tetrafluoroborate, undergo oxidation to the corresponding ketones *via* hydride abstraction.[1,2] As this process can be rationalized on the basis of stabilization of the carbonium ion β to the trimethylsilyl group as a result of C-Si σ-π conjugation[1,3] we expected that a similar result could be achieved using the more stable *tert*-butyldimethylsilyl ethers.[4] Surprisingly, when testosterone *tert*-butyldimethylsilyl ether (1a)[5] was treated with trityl tetrafluoroborate in methylene chloride solution (25°, 1 hour) followed by aqueous workup, the only steroidal product detectable by tlc was the hydrolysis product testosterone (1b) and not the expected product of oxidation, androst-4-ene-3,17-dione (2). The β-diketone 3a[6] underwent a similar transformation as did the less hindered *tert*-butyldimethylsilyl ether 4a[5] to give the hydrolyses products 3b and 4b, respectively. The *tert*-butyldimethylsilyl ethers 5a[5] and 6a[6] were also susceptible to hydrolysis giving the primary alcohols 5b and 6b.

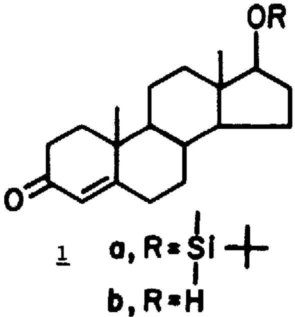
Gas chromatographic analysis of the reaction products after aqueous workup using 1a as a substrate demonstrated that the trityl cation had been converted to triphenylcarbinol and not to triphenylmethane suggesting that the cleavage of the *tert*-butyldimethylsilyl ether was effected by the tetrafluoroborate ion.[7] We have confirmed this is the case as the same transformations can be achieved using lithium tetrafluoroborate. In fact, this method is a viable alternative to the usual tetra(n-butyl)ammonium fluoride or acid hydrolysis conditions.[4] As shown in Table 1, generation of both primary and secondary alcohols from their corresponding *tert*-butyldimethylsilyl ethers can be achieved using either trityl tetrafluoroborate in methylene chloride or lithium tetrafluoroborate in acetonitrile-methylene chloride mixtures. It is noteworthy that β-diketone 6b could not be satisfactorily prepared from 6a using either tetra(n-butyl)ammonium fluoride or acid conditions.

Table 1

Substrate	Product[8]	Yield % using $(C_6H_5)_3BF_4$;	$LiBF_4$
1a	1b	75	78
3a	3b	78	78
4a	4b	50	71
5a	5b	40	40
6a	6b	51	86

In a typical example, the silyl ether 6a (5.51 g, 10.00 mmole) was dissolved in dry methylene chloride (200 ml) and dry acetonitrile (125 ml) added until the solution became turbid. Additional methylene chloride (40 ml) was added to the reaction mixture to remove the turbidity followed by the addition of lithium tetrafluoroborate (2.82 g, 30.00 mmole). The reaction mixture was then stirred at room temperature for sixty hours, diluted with methylene chloride at the end of this time period and washed with water, saturated aqueous $NaHCO_3$ and finally brine. The organic layer was dried over $MgSO_4$ and concentrated to give a tan solid. Recrystallization from methylene chloride/heptane gave 6b (3.76 g, 86% yield), m.p. 234-236°C.

As fluoride transfer from tetrafluoroborate anions to electron deficient centers is known,[9] the cleavage of tert-butyldimethylsilyl ethers can be rationalized as donation of fluoride to silicon directly from BF_4^-, resulting in formation of an $OBF_3^{\ominus}$ species.



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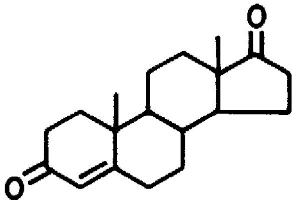

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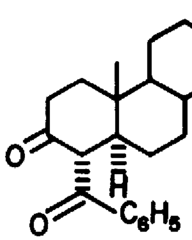

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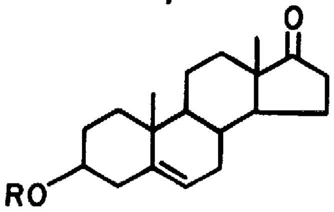

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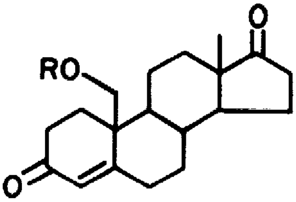

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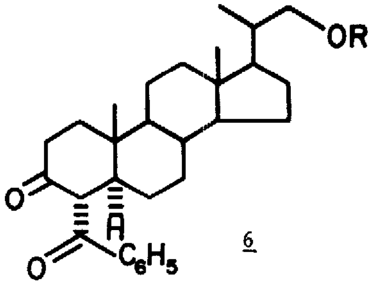

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References

1. M. E. Jung, J. Org. Chem., 41, 1479 (1976).
2. M. E. Jung and L. M. Speltz, J. Amer. Chem. Soc., 98, 7882 (1976).
3. W. Hanstein, H. J. Berwin, and T. G. Traylor, J. Amer. Chem. Soc., 92, 829 (1970).
4. E. J. Corey and A. Venkateswarlu, J. Amer. Chem. Soc., 94, 6190 (1972).
5. The tert-butyldimethylsilyl ether was prepared according to Reference 4.
6. B. W. Metcalf, K. Jund and J. Burkhart, Tetrahedron Letters, in press.
7. The cleavage of tert-butyldimethylsilyl ethers with boron trifluoride etherate has recently been reported, D. R. Kelly, S. M. Roberts, and R. F. Newton, Synth. Comm., 9, 295 (1979).
8. Product identities except for 3b and 6b which were unknown were confirmed by mixed m.p. determinations with reference samples.
9. M. P. Doyle, J. L. Whitefleet and R. J. Bosch, J. Org. Chem., 44, 2923 (1979).

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