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Use of Trimethylsily! Derivatives in Simple Syntheses of Deuteriated Anilines, Phenols, and Benzenethiols

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Deuteriated anilines, XC₆H₄·ND₂, phenols, XC₆H₄·OD, and benzenethiols, XC₆H₄·SD, of high isotopic purity have been obtained in excellent yield from deuteriomethanol, MeOD, and the appropriate trimethylsilyl derivatives, $XC_{6}H_{4} \cdot N(SiMe_{3})_{2}$, $XC_{6}H_{4} \cdot O \cdot SiMe_{3}$, and $XC_{6}H_{4} \cdot S \cdot SiMe_{3}$.

N-DEUTERIATED anilines of high isotopic purity have usually been prepared by hydrogen exchange (e.g., by repeatedly shaking aniline with deuterium oxide¹ or deuteriated alkali² under heterogeneous conditions), a method which is both time-consuming and wasteful of deuterium since the process must be repeated several times if >99% N-deuteriation is required. (Catalytic reduction of the appropriate nitro-compound with deuterium gas,³ which has also been used for aniline, is unnecessarily complicated, would clearly not be suitable for certain substituted anilines, and might lead to unwanted incorporation of deuterium into the aromatic ring.) Hydrogen exchange is equally unsatisfactory for the preparation of O-deuteriated phenols and S-deuteriated benzenethiols.4

Most compounds containing silicon-nitrogen bonds react readily with simple alcohols to give silicon alkoxides and the free amines,⁵ and we have utilized this reaction to provide a simple synthesis of deuteriated amines. For example, brief refluxing of a solution of NN-bistrimethylsilylaniline in O-deuteriomethanol gives methoxytrimethylsilane and NN-dideuterioaniline of >99% isotopic purity. The deuterioaniline is generated in virtually quantitative yield, and there is little loss of deuterium since the mixture of residual deuteriomethanol and methoxytrimethylsilane can be distilled off for reuse. A list of substituted NN-dideuterioanilines, $XC_{6}H_{4}ND_{2}$, prepared in this way is given in the Table; mass spectrometry showed that the isotopic purity was >99% in all cases. For sterically hindered silylamines, a trace of acid may be added to the reaction mixture, since the methanolysis is catalysed very strongly by acid, but not by alkali.6

O-Trimethylsilylphenols and S-trimethylsilylbenzenethiols undergo analogous deuteriomethanolysis to give high yields of deuterio-phenols and -benzenethiols of >99% isotropic purity; examples are given in the Table.

EXPERIMENTAL

NN-Bistrimethylsilylanilines.-n-Butyl-lithium in hexane (180 ml; 1.6M) was added to aniline (11.7 g, 0.125 mol) in

¹ A. Murray and D. Williams, 'Organic Syntheses with Isotopes,' Interscience, New York, part II, 1958; S. Califano and R. Moccia, *Gazzetta*, 1957, **87**, 805.

² A. Brodskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1949, 3 (*Chem. Abs.*, 1949, **43**, 5071). ³ L. Line, B. Wyatt, and H. Smith, *J. Amer. Chem. Soc.*,

1952, 74, 1808.

⁴ C. Bell and G. Barrow, *J. Chem. Phys.*, 1959, **31**, 1158; D. Earnshaw, G. Cook, and G. Dinneen, *J. Phys. Chem.*, 1964, **68**, 296; M. Koizumi and T. Titani, *Bull. Chem. Soc. Japan*, 1939, 14, 40.

ether (100 ml) and the mixture was boiled under reflux for 30 min. Chlorotrimethylsilane (45 g, 0.4 mol) was added, and the mixture was boiled for an additional 6 h, then filtered under dry nitrogen. Fractionation of the filtrate gave NN-bistrimethylsilylaniline (21 g, 70%), b.p. $54^{\circ}/1.0$

Deuteriated anilines, XC_6H_4 ·ND₂, phenols, XC_6H_4 OD, and benzenethiols, XC_6H_4SD , prepared by deuteriomethanolysis of XC₆H₄N·(SiMe₃)₂, XC₆H₄·O·SiMe₃, and XC₆H₄S·SiMe₃

	Reflux	Yield	$\nu(Z-D)/$	B.p. or m.p.	
х	time/h	(%)	cm-1 a	Found	Lit. ^b
Anilines					
H	1	94	2570,	62°/	184°/
			2430	6 mmHg	760 mmHg •
m-OMe	1	93	2430,	64/	251/
			2390	0.35 mmHg	760 mmHg ⁴
p-Br	1	94	2360,	$64-65^{\circ}$	66·4° °
-			2430		
Phenols					
H	5	95	2500	394 0	43 °
p-Br	5	93	2500	65 - 66	66·4 °
ϕ -SiMe ₃	6	95	2500	72 - 73	74 °
p-NO ₂	6	92	2500	115-116	114 °
Benzeneth	iols				
p-Br	2	92	1950	7475	75°
∲-Cl	2	95	1940	6061	61 °
p-SiMe ₃	2	95	1950	60°/	68°/
• •				0.8 mmHg	1•3 mmHg1

^a Z = N, O, or S. ^b Protium compound. ^c Ref. 12. ^d Dictionary of Organic Compounds, Eyre and Spottiswoode, London, 4th edn., 1965. ^e Ref. 10. ^f Ref. 11.

mmHg, m.p. 16° (lit., b.p. 98-99°/11 mmHg, m.p. 16-17°).

m-Anisidine was similarly converted into NN-bistrimethylsilyl-m-anisidine (70%), b.p. 64°/0.3 mmHg (Found: C, 58.7; H, 9.5. C₁₃H₂₅NOSi requires C, 58.4; H, 9.4%), and p-anisidine into NN-bistrimethylsilyl-p-anisidine (72%), b.p. 68°/0.4 mmHg (Found: C, 58.6; H, 9.6%).

The preparation of p-bromo-NN-bistrimethylsilylaniline has been described previously.8

p-Nitro-O-trimethylsilylphenol.--p-Nitrophenol (10 g, 0.07 mol), chlorotrimethylsilane (15 g, 0.15 mol), and light petroleum (b.p. 100-120°) (30 ml) were heated together under The reaction was judged to be complete after 24 h, reflux. when all the p-nitrophenol, which is practically insoluble in the reaction mixture, had dissolved. The solvent and the excess of chlorotrimethylsilane were then distilled off, and the residue was fractionated under reduced pressure to give

⁵ C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, p. 345.

A. R. Bassindale, C. Eaborn, and D. R. M. Walton, unpublished work.

⁷ U. Wannagat, C. Kruger, and H. Niederprum, Z. anorg. Chem., 1962, **314**, 80.

⁸ D. R. M. Walton, J. Chem. Soc. (C), 1966, 1706.

J. Chem. Soc. (C), 1970

p-nitro-O-trimethylsilylphenol (13.5 g, 90%), b.p. 104°/1.0 mmHg, n_D²⁵ 1.5264 (Found: C, 51.4; H, 6.4. C₉H₁₃NO₃Si requires C, 51.2; H, 6.2%).

Resorcinol was similarly silylated to give OO-bistrimethylsilylresorcinol (91%), b.p. 60°/0·2 mmHg, $n_{\rm D}^{20}$ 1·4750 (lit.,⁹ b.p. $154^{\circ}/100 \text{ mmHg}$, n_{D}^{20} 1.4748). O-Trimethylsilylphenol, b.p. $110^{\circ}/100$ mmHg, $n_{\rm D}^{25}$ 1.4760 (lit., 10 b.p. 81°/23 mmHg, n_D^{20} 1·4782), p-bromo-O-trimethylsilylphenol, b.p. $69^{\circ}/0.1 \text{ mmHg}$, n_{D}^{25} 1.5120 (lit., ¹⁰ b.p. 126°/25 mmHg, n_D^{25} 1.5123), and *p*-O-bistrimethylsilylphenol (b.p. $85^{\circ}/2$ mmHg, $n_{\rm D}^{25}$ 1.4800 (lit.,¹⁰ b.p. 132°/25 mmHg, $n_{\rm D}^{25}$ 1.4794), were prepared as previously described.¹⁰

S-Trimethylsilylbenzenethiols .-- The preparations of the compounds XC_6H_4 ·S·SiMe₃ (X = H, p-Br, p-Cl, or p-SiMe₃) have been described elsewhere.11

Preparation of Deuteriated Compounds.---(i) p-Bromo-NNdideuterioaniline. In a typical procedure, p-bromo-NNbistrimethylsilylaniline (7.9 g, 0.025 mol) was boiled under reflux with O-deuteriomethanol (10 ml) for 1 h. Methoxy-

⁹ S. Langer, S. Connell, and I. Wender, J. Org. Chem., 1958,

23, 30. ¹⁰ J. L. Speier, J. Amer. Chem. Soc., 1952, 74, 1003.

trimethylsilane and deuteriomethanol were distilled off, and the residue was fractionated under reduced pressure to give p-bromo-NN-dideuterioaniline (94%), b.p. 110°/20 mmHg, m.p. 64-65° (lit.,¹² 66·4°), v(ND₂) 2360 and 2430 cm⁻¹.

(ii) OO-Dideuterioresorcinol. OO-Bistrimethylsilylresorcinol (6.3 g, 0.025 mol) was boiled under reflux with excess of O-deuteriomethanol (10 ml) for 6 h and the mixture was distilled to give methoxytrimethylsilane and deuteriomethanol followed by OO-dideuterioresorcinol (92%), b.p. 60°/0•2 mmHg, m.p. 108—109° (lit.,³ 110°), v(O-D) 2500 cm⁻¹.

Details of other preparations are included in the Table. Mass Spectra.-Mass spectra were recorded on an A.E.I. MS9 spectrometer.

We thank the S.R.C. for support, and the Nobel Division of Imperial Chemical Industries, Ltd., for a studentship (to A. R. B.)

[0/137 Received, January 28th, 1970]

¹¹ A. R. Bassindale and D. R. M. Walton, J. Organometallic Chem., in the press. ¹² 'Handbook of Chemistry and Physics,' The Chemical

Rubber Co., Ohio, 46th edn., 1965.