Journal of Organometallic Chemistry, 116 (1976) 153—159

ONE-STEP CONVERSION OF ALKOXYTRIMETHYLSILANES TO ALKYL BENZENESULFONATES

P. YKMAN and H.K. HALL, Jr. *

Department of Chemistry, University of Arizona, Tucson, Arizona 85721 (U.S.A.)

(Received January 9th, 1976)

Summary

Direct conversion of alkoxytrimethylsilanes to alkyl benzenesulfonates was accomplished in one step by treatment with benzenesulfonyl fluoride and catalytic amounts of tetraethylammonium fluoride. The reaction proceeded best when the alkoxygroup carried electron-withdrawing groups such as F or CN. Allyloxytrimethylsilane was smoothly converted to allyl benzenesulfonate. Unsubstituted alkyl groups gave lower conversions. The silyl derivative of acetone cyanohydrin gave no sulfonate, but that of 3-cyanocyclobutanone gave high conversion. An ionic chain mechanism was postulated for these reactions. The same conversions, but without a catalyst, could be accomplished by the benzenesulfonyl halides in general; however, these reactions involved prolonged heating.

Introduction

It would be useful in certain synthesis sequences to be able to convert alcohols (I) to sulfonate esters (III) in the absence of alkali or pyridine. Groups such as ester functions are attacked by alkali, while pyridine is alkylated by reactive benzenesulfonates (Menshutkin reaction). In the present work we describe a two-step sequence involving the preparation of the trimethylsilyl ether (II) and its subsequent direct conversion to benzenesulfonate (III) (eq. 1 and 2).

$$\underset{\text{(I)}}{ROH} \rightarrow \underset{\text{(II)}}{ROSi(CH_3)_3} \qquad (1)$$

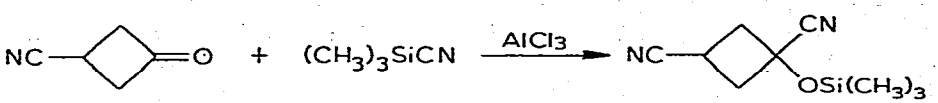
$$\underset{\text{(II)}}{ROSi(CH_3)_3} + C_6H_5SO_2F \xrightarrow{F^-} \underset{\text{(III)}}{ROSO_2C_6H_5} \qquad (2)$$

Reaction 2 may also be used in converting volatile alkoxytrimethylsilanes, of nonvolatile alcohols isolated by distillation or preparative GLC, to the corresponding sulfonates.

Results

Preparation of alkoxytrimethylsilanes

Most of the required alkoxysilanes IIa—IIg (Table 1) have been synthesized previously by a variety of methods [1—4]. We found that reaction of the appropriate alcohol with hexamethyldisilazane was simple and convenient, and gave good yields when electron-withdrawing subsituents were present at the α-, β-, or γ-positions of the alcohol. 1,3-Dicyano-1-trimethylsiloxycyclobutane IIh was prepared in 92% yield by treating 3-cyanocyclobutanone with trimethylcyanosilane with a catalytic amount of aluminum chloride [2].



(IIh)

Reaction of alkoxytrimethylsilanes with benzenesulfonyl fluoride

Alkoxytrimethylsilanes IIa—IIh reacted with benzenesulfonyl fluoride containing a catalytic amount of tetraethylammonium fluoride to give benzenesulfonates IIIa—IIIh (Table 2). Fluoroalkoxysilanes IIb and IIc gave good results (GLC yields 100% and 95%, respectively, isolated yields 70% and 47%, respectively), as did the 3-cyanocyclobutyloxysilane IIa (isolated yield 44%). Poorer conversion to benzenesulfonate was obtained when the alkyl groups were methyl IIf (NMR yield 69%, isolated yield 23%), n-butyl IIg (NMR yield 66%, isolated yield 28%), and allyl IIe (NMR yield 40%, isolated yield 28%).

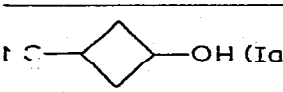
2-Cyano-2-propoxytrimethylsilane IId failed to give a sulfonate, acetone being the only detected product. In contrast, 1,3-dicyanocyclobutyloxytrimethylsilane IIh gave the sulfonate IIIh, isolated in 61% yield.

Comparison with non-catalyzed benzenesulfonylation

We were interested to discover whether other bezenesulfonylating agents could

TABLE 1

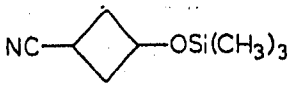
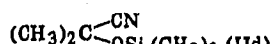
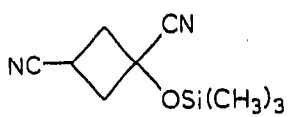
CONVERSION OF ALCOHOLS ROH (I) TO ALKOXYTRIMETHYLSILANES ROSi$(CH_3)_3$[a] (II)

Alcohols	B.p. of silyl derivative II (°C) (literature b.p.)	Yield (%)
 (Ia)	54—56/0.5 mmHg	82[b]
CF_3CH_2OH (Ib)	76—77	51[b]
$(CF_3)_2CHOH$ (Ic)	85—86 (86 [1])	57
$(CH_3)_2C(CN)OH$ (Id)	145—147 (145.5—147 [2])	76
$CH_2=CHCH_2OH$ (Ie)	92—96.5 (100 [3])	53

[a] All reactions at room temperature with a 2 : 1 mol ratio alcohol/hexamethyldisilazane; for Ib a 2 : 1.1 ratio was used. All the reactions were exothermic. [b] See Experimental section.

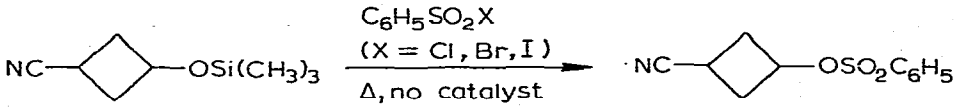
TABLE 2

CONVERSION OF ALKOXYTRIMETHYLSILANES ROSi$(CH_3)_3$ (II) TO ALKYLBENZENESULFONATES $ROSO_2C_6H_5$[a] (III)

Alkoxytrimethylsilane	Reaction time	B.p. or m.p. of the alkylbenzenesulfonate (III)	Yield by NMR/GLC (%)	Isolated yield (%)	Lit. b.p. or m.p. of III (°C)
 (IIa)	10 min	undistillable oil [6]		44	undistillable oil [6]
$CF_3CH_2OSi(CH_3)_3$ (IIb)	5 days	72 (0.09 mmHg)		70	91 (1 mmHg) [7]
$(CF_3)_2CHOSi(CH_3)_3$ (IIc)	3 wks	58 (0.4 mmHg)	95	47	
 (IId)				0[b]	
$CH_2=CHCH_2OSi(CH_3)_3$ (IIe)	1 day	89—92 (0.07 mmHg)	40	28	
$CH_3OSi(CH_3)_3$ (IIf)	1 day 1 day[c] 6 days[c] 4 wks[c]	75 (0.3 mmHg)	69 69[c] 77[c] 88[c]	23	115 (4 mmHg) [8]
$n\text{-}C_4H_9OSi(CH_3)_3$ (IIg)	4 days[d]	109 (0.4 mmHg)	66	28	147—148 (4 mmHg) [8]
 (IIh)	6 days	e		61	

[a] All reactions were performed at room temperature unless otherwise indicated, using a 1 : 1 : 0.1 mol ratio of silyl ether/benzenesulfonyl fluoride/tetraethylammonium fluoride. [b] Acetone was the only product identified. [c] KF with 18-crown-6 in acetonitrile at r.t. [d] Refluxing acetonitrile. [e] Two isomers; one was isolated alone (m.p. 69.5—70°C); the second one (always contaminated by the first one) was an oil. See Experimental section.

convert alkoxytrimethylsilanes to benzenesulfonates. Heating IIa with benzenesulfonyl chloride for 3 days at 150°C gave IIIa in 80% yield. Benzenesulfonyl bromide converted IIa to IIIa in 88% yield in a reaction carried out for 1 day at 115°C. Reaction of benzenesulfonyl iodide with IIa gave a 36% yield of IIIa after 1 day at 28°C; in this experiment side reactions are responsible for the low yield.



(IIa) (IIIa)

Discussion

Scope of the reaction

We have demonstrated that alkoxytrimethylsilanes give good conversions to alkyl benzenesulfonates when treated with benzenesulfonyl fluoride and tetraethylammonium fluoride if the alkyl groups contain electron-withdrawing substituents. The reactions proceed cleanly and under mild conditions. The yields were lower for unsubstituted alkoxytrimethylsilanes. The reaction allowed us to synthesize the new, reactive allyl benzenesulfonate. Our preparation of 1,3-dicyanocyclobutyl benzenesulfonate (overall yield 56%) is an improvement of that previously reported [9] (45%) and also avoids the use of poisonous hydrogen cyanide.

The stability of the alkoxy anion must be an important factor since, as mentioned above, alkoxy groups containing electron-withdrawing substituents gave best results. Structural factors also play a role. Whereas 2-cyano-2-propyloxytrimethylsilane gave only acetone, 1,3-dicyanocyclobutyloxytrimethylsilane gave the expected benzenesulfonate in good yield. Although the extra nitrile group in IIh plays some role, the major factor is presumably the relutance of the 1,3-dicyanocyclobutoxide ion to elimate cyanide ion to form the highly strained cyclobutanone.

It was shown that the same conversion could be accomplished by non-catalyzed reactions with benzenesulfonyl halides. However, the latter requires prolonged heating to bring about high conversion.

We favor an ionic chain mechanism for reactions 2a and 2b.

$$ROSi(CH_3)_3 + F^- \rightarrow RO^- + (CH_3)_3SiF \quad (2a)$$

$$RO^- + C_6H_5SO_2F \rightarrow ROSO_2C_6H_5 + F^- \quad (2b)$$

The chain-carrying fluoride ion, originally supplied by tetraethylammonium fluoride, combines with silicon to release an alkoxide ion. This reaction has already been demonstrated by Corey and Snider [10], who utilized tetrabutylammonium fluoride to desilylate several siloxy compounds. The high affinity of silicon for fluoride provides the basis for this reaction. In the second step the alkoxide ion attacks benzenesulfonyl fluoride to form benzenesulfonate and regenerate fluoride ion. A similar mechanism has been proposed by Niederpruem, Voss, and Beyl [11] for the reaction of silylated phenols with perfluorosulfonyl fluorides.

A likely chain-breaking step is the reaction of fluoride ion with alkyl benzenesulfonate (eq. 2c).

$$F^- + ROSO_2C_6H_5 \rightarrow RF + \bar{O}_3SC_6H_5 \quad (2c)$$

Conclusion

Our work shows that siloxy derivatives of relatively acidic alcohols can be efficiently converted to the corresponding sulfonate esters by benzenesulfonyl fluoride with fluoride ion as a catalyst. The synthetic utility of the reaction has been demonstrated in the preparation of IIIh and of allyl benzenesulfonate IIIe.

Experimental section

General

All boiling points and melting points are uncorrected. Capillary melting points were determined on a Thomas—Hoover melting point apparatus. Infrared spectra were determined with a Perkin—Elmer Model 337 spectrophotometer in KBr or between NaCl plates (the wavelengths are given in cm^{-1}). NMR spectra were obtained on a Varian T60 spectrometer. Chemical shifts are reported on the τ-scale (ppm). The gas chromatograms were obtained on a Varian Aerograph 1700 instrument using the following column: 3% SE30 on 80-100 mesh Chromosorb W AW/DMCS HP, 5 ft x 0.25 in.

Representative alkoxytrimethylsilane synthesis

3-Trimethylsiloxycyclobutanecarbonitrile (IIa). In a 3-necked flask fitted with a nitrogen inlet, drying tube, and magnetic stirring bar was placed 0.1 g. of ammonium chloride and 9.7 g. (0.1 mol) of freshly distilled 3-cyanocyclobutanol [9]. Addition, under nitrogen, of 8.05 g. (0.05 mol) of hexamethyldisilazane (Aldrich) resulted in an instantaneous, exothermic reaction. After 10 min the reaction was finished, as evidenced by the end of ammonia evolution. Filtration and distillation of the filtrate gave 10.7 g. (60%) of 3-cyanocyclobutoxytrimethylsilane, IIa, b.p. 54—56°C (0.5 mmHg). (Found: C, 56.69; H, 8.95; Si, 16.33. $C_8H_{15}NOSi$ calcd.: C, 56.80; H, 8.87; Si, 16.57%.) IR(NaCl, neat) 2250(—C≡N), 1250, 840, and 755 (all Me_3Si). NMR(CCl_4); 5.7—6.1 (m,1), 6.7—8.2(m,5), 9.95(s,9,Me_3Si). When the ammonium chloride was omitted, a 30 min reaction time was required, but the filtration step was unnecessary. A 13.9g (82%) product was obtained.

2,2,2-Trifluoroethoxytrimethylsilane (IIb). 2,2,2-Trifluoroethanol, 20g (200 mmol) and 17.7g (110 mmol) of hexamethyldisilazane were placed in a flask fitted with a reflux condenser. The mixture was stirred under nitrogen to mix the two layers, and a strongly exothermic reaction occurred. After two hours most of the ammonia had evolved and the mixture was distilled. After a forerun, the product, contaminated by 5% of a higher-boiling material, 17.55g (51%), distilled at 77—87°C. Redistillation gave pure IIb, b.p. 76—77°C. (Found: C, 34.52; H, 6.26. $C_5H_{11}F_3OSi$ calcd.: C, 34.87; H, 6.44%.) IR (NaCl, neat) 1253 and 843 (Me_3Si). NMR (CCl_4, C_6H_6 as internal standard) 6.03 (q, J 8.6 Hz, 2, CH_2CF_3) and 9.70 (s, 9, Me_3Si).

1,3-Dicyanocyclobutyloxytrimethylsilane (IIh). In a 100 ml flask fitted with a reflux condenser and magnetic stirring bar was placed 19 g. (200 mmol) of 3-cyanocyclobutanone [8] and 20.79 g. (210 mmol) of trimethylcyanosilane [11]. A pinch of aluminum chloride on a spatula tip was added and stirring was started. Immediate heat evolution occured and the flask was cooled in a water bath. After two hours, the mixture was distilled to give, after a small amount of unreacted ketone, 4.35 g of 97.5% pure product (b.p. 119—121°C/5 mmHg, 11% yield) and 31.5 g of 100% pure product (b.p. 121—127.5°C/5 mmHg, 81% yield. (Found: C, 55.47; H, 7.25; N, 14.49. $C_9H_{14}N_2SiO$ calcd.: C, 55.64; H, 7.26; N, 14.42%.) IR (NaCl neat) 2225 (—C≡N, s), 1250, 839 and 754 (MeSi). NMR (CCl_4, C_6H_6 internal reference) 6.57 to 7.52 (m,5) and 9.62 (s, 9, Me_3SiO).

Representative sulfonate synthesis

1,1,1,3,3,3-Hexafluoro-2-propyl Benzenesulfonate (IIIc). To 0.15 g (1.0 mmol) of tetraethylammonium fluoride (Eastman Kodak Co., used without purification but handled in a glove box under argon or nitrogen) was added, in the order shown, under argon 1.60 g. (10 mmol) of benzenesulfonyl fluoride and 2.40 g. (10 mmol) of 1,1,1,3,3,3-hexafluoro-2-propoxytrimethylsilane. The mixture was stirred and the reaction was followed by GLC. After 3 weeks more than 95% of the sulfonyl fluoride was converted to the sulfonate. Ether, 10 ml, was added and the mixture was washed twice with 10 ml of water, dried over magnesium sulfate and filtered. The filtrate was evaporated and distilled under reduced pressure to give, after some sulfonate contaminated by benzenesulfonyl fluoride, the pure sulfonate (1.45 g, 47% yield); b.p. 58°C/0.4 mmHg. (Found: C,35.08; H, 2.09. $C_9H_6F_6O_3S$ calcd.: C, 35.07; H, 1.96%.) IR(NaCl neat) 1375 (SO_2). NMR ($CDCl_3$) 1.88—2.63 (5, typical for monosubstituted phenyl), 4.70 (septet, *J* 9.5 Hz, 1, CHO).

Allyl Benzenesulfonate (IIIe). In a 25 ml flask fitted with an efficient reflux condenser was placed successively 0.45 g. (3 mmol) of tetraethylammonium fluoride, 4.8 g. (30 mmol) of benzenesulfonyl fluoride, and 4.11 g. (31.5 mmol) of allyloxytrimethylsilane. A rapid reaction with heat evolution occurred. The mixture was stirred overnight. Longer reaction times did not increase the conversion over 40%. The mixture was diluted with 50 ml of ether and was washed three times with 30 ml portions of water, dried over magnesium sulfate, filtered, and evaporated. The residue was distilled with a short-path distillation apparatus. Following a forerun of 1.43 g. of benzenesulfonyl chloride, there was obtained 1.68 g. (28%) of pure allyl benzenesulfonate, b.p., 89—92°C (0.07 mmHg). (Found: C, 54.47; H, 5.15. $C_9H_{10}O_3S$ calcd: C, 54.53; H, 5.08%.) IR (NaCl, neat) 1635 (C=C), 1355 and 1200 (SO_2O). NMR ($CDCl_3$) 1.98—2.71 (5, typical for C_6H_5X), 3.83—4.98 (m, 3, CH_2=CH—) and 5.46 (d, *J* 5 Hz, further split, 2, CH_2O).

1,3-Dicyano-1-benzenesulfonyloxycyclobutane (IIIh). In a 250 ml flask equipped with nitrogen inlet and a stirring bar were placed 2.23 g of tetraethylammonium fluoride (15 mmol), 24.64 g of benzenesulfonyl fluoride (154 mmol) and 31.5 g of 1,3-dicyano-1-trimethylsiloxycyclobutane (162 mmol) with vigorous stirring. There was immediate heat evolution and after 40 min a supernatent layer, formed mostly of trimethylfluorosilane, appeared. The mixture was stirred for 6 days. 200 ml of ether was added and the solution was washed

with 70 ml of water, which was backwashed with 100 ml and 50 ml of ether. The combined ether layers were washed twice with 70 ml of water, dried over magnesium sulfate, filtered and evaporated. Some of the benzenesulfonate precipitated in the residue. The mixture was heated under high vacuum to remove the unreacted benzenesulfonyl fluoride. Treatment with water and ether gave a white solid, which consisted mainly of one of the isomers of the product; more solid precipitated from ether. The combined solid fractions were dissolved in chloroform, washed with water and dried over magnesium sulfate. Evaporation gave 17.5 g of moist solid (nearly only one isomer); the remaining oil was heated under high vacuum to remove the remaining benzenesulfonyl fluoride and gave 7.34 g of product (two isomers). The total yield was 24.80 g (61%). The solid can be recrystallized from chloroform/ether to give one isomer in pure form (m.p. 69.5—70°C). The spectral and elemental analyses were performed on a mixture of isomers. (Found: C, 54.73; H, 3.97; N, 10.90. $C_{12}H_{10}N_2O_3S$ calcd: C, 54.95; H, 3.84; N, 10.68%.) IR (NaCl, neat): 2235 (—C≡N) s 1365 and 1185 (SO_2). NMR ($CDCl_3$) 1.87—2.60 (5, 2 multiplets, typical for C_6H_5X), 6.33—7.20 (m, 5 with a large singlet at 6.83).

Reaction of 3-cyanocyclobutyloxytrimethylsilane with benzenesulfonyl halides

This compound was chosen for comparison studies because its high boiling point permitted lengthy thermal reactions. The purity of the benzenesulfonate product IIIa, after purification, was confirmed by the identity of its infrared and NMR spectra with those of the authentic, analytically pure material [6]. Purification, in the benzenesulfonyl fluoride reaction, involved distillation of unreacted benzenesulfonyl fluoride in vacuum, taking up the residue in ether and water, separating ether layer, drying, and evaporating. Reaction mixtures from the other halides were handled similarly except that excess halide was removed by hydrolysis with cold saturated sodium carbonate solution.

Acknowledgments

We are indebted to the U.S. Army Research Office (Durham) for financial support of this work and to the Fulbright—Hays Foundation and the Nato for travel grants to P. Ykman for the academic years 1972—1973 and 1974—1975.

References

1 W.R. Cullen and G.E. Stran, Inorg. Chem., 4 (1965) 1437.
2 W. Lidy and W. Sundermeyer, Chem. Ber., 106 (1973) 587; for addition of trimethylcyanosilane to carbonyl, see also: D.A. Evans and L.K. Truesdale, Tetrahedron Lett., 4929 (1973); D.A. Evans, J.M. Huffman and L.K. Truesdale, J. Amer. Chem. Soc., 95 (1973) 5822; D.A. Evans, G.L. Carrol and L.K. Truesdale, J. Org. Chem., 39 (1974) 914; H. Neef and R. Mueller, J. Prakt. Chem., 315 (1973) 367; U. Hertenstein and S. Hünig, Angew. Chem., 87 (1975) 195.
3 T. Takanati, Nippon Kagaku Zasshi, 76 (1955) 9; C.A., 51 (1957) 17724.
4 S.H. Langer, S. Connell and I. Wender, J. Org. Chem., 23 (1958) 50.
5 D. Seyferth, J.E. Hallgren and P.L.K. Hung, J. Organometal. Chem., 50 (1973) 265.
6 H.K. Hall, Jr., unpublished results.
7 E.T. McBee, D.H. Campbell and C.W. Roberts, J. Amer. Chem. Soc., 77 (1955) 3149.
8 C.D. Nenitzescu, V. Ioan and L. Teodorescu, Chem. Ber., 90 (1957) 585.
9 H.K. Hall, Jr., E.P. Blanchard, Jr., S.C. Cherkofsky, J.B. Sieja and W.A. Sheppard, J. Amer. Chem. Soc, 93 (1971) 110.
10 E.J. Corey and B.B. Snider, J. Amer. Chem. Soc., 94 (1972) 2549. E.J. Corey and A. Venkateswarlu, ibid., 94 (1972) 6190; for limitations of this method see G.H. Dodd, B.T. Golding and P.V. Ioannou, J. Chem. Soc., Chem. Commun., 249 (1975).
11 H. Niederpruem, P. Voss and V. Beyl, Justus Liebigs Ann. Chem., (1973) 20.
12 J.W. Zubrick, B.I. Dunbar and H.D. Durst, Tetrahedron Lett., 71 (1975).