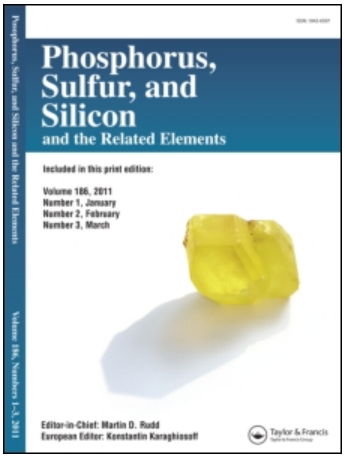

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ON THE BEHAVIOUR OF SULFONATES TOWARDS AS(III) NUCLEOPHILES

Gerasimos M. Tsivgoulis[a]; Demetrios N. Sotiropoulos[a]; Panayiotis V. Ioannou[a]
[a] Department of Chemistry, University of Patras, Patras, Greece

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ON THE BEHAVIOUR OF SULFONATES TOWARDS AS(III) NUCLEOPHILES

GERASIMOS M. TSIVGOULIS, DEMETRIOS N. SOTIROPOULOS and PANAYIOTIS V. IOANNOU*

Department of Chemistry, University of Patras, Patras, Greece

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Mesylates and hydrophilic amsylates and [3]betylates were tried as substrates in an effort to create a C-As bond. In no case did we detect the formation of arsonic acids. With Na_3AsO_3 as nucleophile the product was the parent alcohol due to exclusive attack of the HO^- present in the aqueous Na_3AsO_3. With $(PhS)_3As$ as the nucleophile in the absence of Lewis acid catalyst the products were diphenyl disulfide and As_2O_3 while in the presence of catalyst alkyl phenyl sulfide was obtained, implying that the electron pair on As was chemically inactive. As_2O_3 did not react with these electrophiles, and potassium di-O-phenylenedioxyarsenate(III) was unreactive towards alkyl bromides but it gave the monoalkyl ether of catechol with amsylates and [3]betylates, again implying that the stereochemically active electron pair of As was not chemically active.

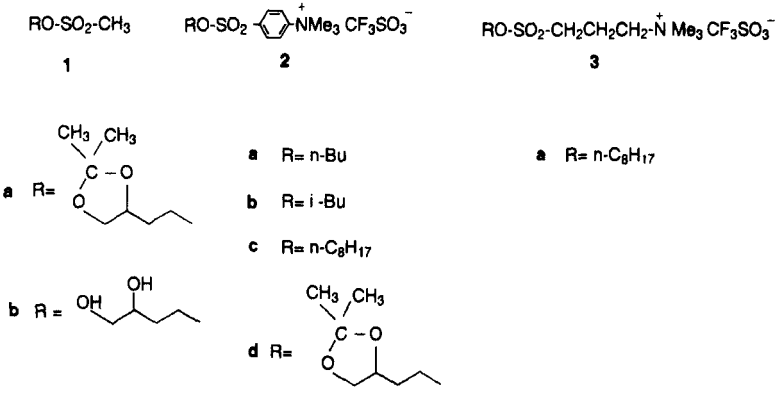
Keywords: the Meyer reaction; mesylates; amsylates; betylates; sodium arsenite; triphenyl trithioarsenite; di-O-phenylenedioxyarsenate(III)

INTRODUCTION

The Meyer reaction[1], i.e. the displacement of a *halide* ion by AsO_3^{3-} nucleophile[2] to give an aliphatic arsonic acid, is one technique for creating a C-As bond.[3] The yields depend on the hydrophilicity of the alkyl halide (the more lipophilic the lower the yield), and the reaction conditions.[4,5]

When the substrate for the Meyer reaction is soluble in the aqueous Na_3AsO_3, then the reaction is simple in practice and the yields are very satisfactory. Such substrates are 3-chloropropane-1,2-diol,[6], glycidol,[7,8], ethylene oxide,[9], and 2-halocarboxylic acids,[3,10] but afford specific arsonic acids thus lacking the required generality for creating a C-As bond *via* the Meyer reaction.

We thought that a *hydrophilic* leaving group may impart enough aqueous solubility to a substrate to give the Meyer reaction. Sulfonates are better leaving groups than halides[11] and are prepared from substrates bearing the -OH group which is found in biologically relevant molecules. Moreover, when the sulfonate is converted to a cation then the sulfonate becomes an even better leaving group and at the same time imparts aqueous solubility to the substrate.



We, therefore, selected mesylates, **1** (as more hydrophilic than tosylates), amsylates,[12,13], **2**, and [3]betylates,[14] **3**, as substrates for the Meyer reaction, and herein we report their behaviour on Na_3AsO_3, As_2O_3, triphenyl trithioarsenite, **4**, and potassium di-O-phenylenedioxyarsenate (III), **7**.

RESULTS AND DISCUSSION

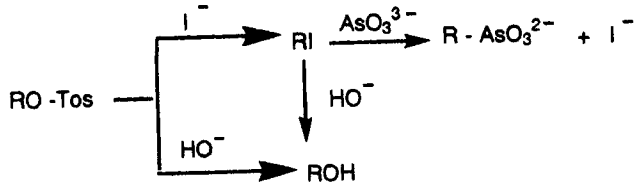
For the esterification of sulfonyl chlorides with the alcohols we generally used the method of Timpson,[15] where the sulfonyl chloride is added to a cooled solution of the alcohol in pyridine. Derivatives of butane-1,3,4-triol were prepared and tried in the Meyer reaction because of the poor yields obtained, under various conditions, for the preparation of *rac*-3,4-dihydroxybutylarsonic acid.[16] The compounds **1b** and **2d** were not stable. Instability was also noted for 3,4-dihydroxybutyl bromide,[16,17] tetrahy-

dropyranyl ether of 3,4-dihydroxybutyl bromide[16] and isopropylidene ketal of 3,4-dihydroxybutyl bromide.[16]

The reaction of **1b** with Na_3AsO_3 gave butane-1,3,4-triol and no arsonic acid nor 3-hydroxytetrahydrofuran. The behaviour of the mesylate **1b** towards Na_3AsO_3 contrasts that of 3,4-dihydroxybutyl bromide which gave the arsonic acid, 3,4-dihydroxybutylarsonic acid, and 3-hydroxytetrahydrofuran, as a by-product.[16] It seems that the mesylate is attacked by the HO^- and not by the AsO_3^{3-} nucleophile ($HAsO_3^{2-}$ has no nucleophilic activity[2]):

$$AsO_3^{3-} + H_2O \Leftrightarrow HAsO_3^{2-} + HO^- \qquad (1)$$

The fully blocked mesylate **1a** was also nonreactive towards Na_3AsO_3. Small amounts of butane-1,3,4-triol were detected by TLC arising from the HO^- nucleophile. It seems therefore that the *neutral* sulfonates do not give the Meyer reaction. However, methyl and ethyl tosylates give the Meyer reaction in 50% yields in the presence of catalytic amounts of NaI.[18] Obviously, the reaction goes *via* the iodide and not *via* the tosylate:



(2)

When **1a** was reacted with Na_3AsO_3 in the presence of 20 or 40% NaI virtually no arsonic acid was produced. TLC revealed the presence of **1a,** butane-1,3,4-triol and traces of isopropylidene ketal of 3,4-dihydroxybutyl iodide. Evidently, the difference in reactivity between the methyl and ethyl tosylates and **1a** must be due to insolubility of the latter in the aqueous Na_3AsO_3.

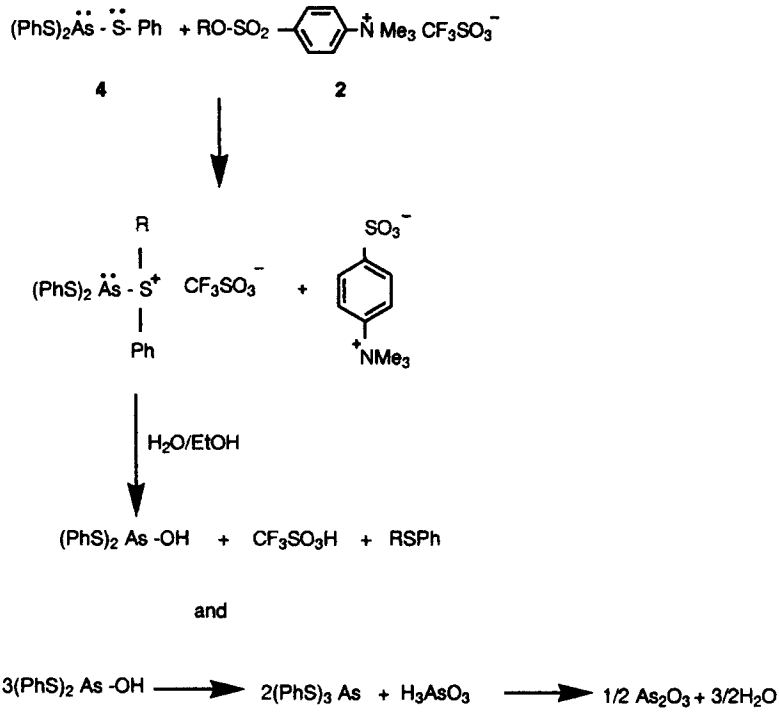
Using a variety of conditions, in no case did we obtain arsonic acids in the reaction of the more hydrophilic sulfonates **2a-2d** or **3a** with Na_3AsO_3. The only product was the parent alcohol arising from the attack of HO^- nucleophile. No alkenes were detected by TLC. When NaI was used as a catalyst, no arsonic acid was produced; the products being the parent alcohol (major) and its iodide (minor product).

King et al.[14] conducted the Arbuzov reaction using a [2]betylate and triethyl phosphite and he also obtained the phosphonium salt with triphenylphosphine. Triesters of As(III) do not give reactions analogous to the Arbuzov reaction due to the reduced nucleophilicity of As compared to P.[19] The nucleophilicity of As(III) should increase in the series $(RO)_3As \cong H_3AsO_3$, $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-} and this was indeed found.[2] Therefore AsO_3^{3-} should be nucleophilic towards sulfonates. That it is not, is probably due to steric reasons due to the bulkier $-OSO_2R'$ group. In this case the electrophilic carbon atom is not able to adopt the trigonal bipyramidal configuration, required for the S_N2 mechanism, with both AsO_3^{3-} and $-OSO_2R'$ at the apical positions. This is not the case with I^- or HO^- nucleophiles because reactions (2) take place with I^- catalysis and we observed solvolysis of charged sulfonates.

Chadaeva et al.[20] found that methyl iodide was inactive towards triphenyl trithioarsenite, **4,** while it was active[21] towards dialkyl alkyldithioarsonite, $RAs(SR')_2$, the S atoms being the nucleophilic centers and not the As atom. We found that **4** and **2c** in CH_2Cl_2 reacted smoothly giving As_2O_3 and diphenyl disulfide without using up the **2c.** Since **4** alone was stable under the same conditions, it seems that **2c** catalysed the oxidation of **4** by atmospheric O_2, by an unknown mechanism. When the reaction was carried out in benzene solution in the presence of $AlCl_3$, all the ester reacted giving octyl phenyl sulfide. In this case, too, the lone pair of electrons on As was not reactive. A plausible mechanism is shown in Scheme 1.

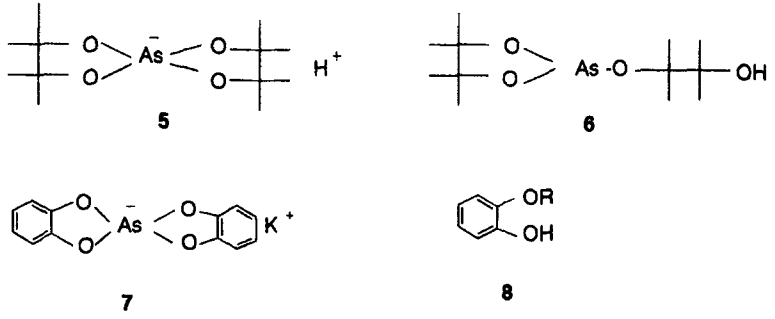
As_2O_3 does form a complex with $BF_3{\cdot}Et_2O$ as evidenced by the change in the texture of the crystals but on drying in vacuo As_2O_3 was recovered. $BF_3{\cdot}Et_2O$ also complexes with **2c** giving a stable towards drying complex, **2c**·3.5BF_3, as an oil, which on hydrolysis gave the octyl amsylate as the borate salt. As_2O_3 does not react with **2c** either alone or in the presence of $BF_3{\cdot}Et_2O$. In the later case, after hydrolysis, part of the amsylate precipitates as the borate salt and part remains as the triflate salt, **2c.**

Complexes of As(III) with diols, like pinacol,[22] **5** or catechol,[23] **7,** have a negatively charged As atom which in principle should have nucleophilic activity. We tried to prepare the complex **5** according to Englund[22] but we found that it had the structure **6.** The ester structure **6** explains the observation[22] that "the compound dissolves in pyridine and aniline and from the solutions the original compound crystallizes". The ester, as Englund also noted[22], did not react with alkyl halides. Attempts



SCHEME I

towards the cyclization of **6** to the sodium salt of **5** using NaH were unsuccessful.



The structure of the complex **7** is known.[24] In the solid state the electron pair on As is stereochemically active, forming the fifth apex of a distorted trigonal bipyramid. The question, now, is whether it is also chemically active. Complex **7** was unreactive with alkyl bromides under various conditions. However, it reacted with **2c** and with **3a** at 50°C for 9–12 h but the product was not the anticipated (after hydrolysis) arsonic acid but the monooctyl ether of catechol, **8.** In these cases, too, the electron pair of arsenic was not chemically active compared to that of oxygen. The latter attacks the electrophiles **2c** or **3a** to give, after work up, the observed product. 5–10% octanol was detected by TLC and it arose from the presence of moisture in the complex **7.**

EXPERIMENTAL

The starting compounds and reagents for the syntheses of sulfonates were from Aldrich. Known compounds were prepared according to the literature: *rac*-1,2-O-isopropylidenebutane-1,2,4-triol[25] (b.p. 66–7°C/0.8 mm Hg), the alkyl p-trimethylammoniumbenzenesulfonate triflates **2a**[12] (m.p. 135–6°C), **2b**[12] (m.p. 91–2°C dec.), **2c**[12] [m.p. 83–5°C; TLC: R_f 0.65 in $CHCl_3$/MeOH 1:1; IR (KBr) : 2926 (s), 1370 (m), 1258 (vs), 1184 (s), 1160 (s), 1034 (m), 950 (s), 850 (s), 644 (s), 572 (m)], 3-chloropropanesulfonyl chloride[14] (b.p. 120–4°C/20 mm Hg; lit.[14] 102–5°C/55 mm Hg), N-methylpropanesultam,[14] octyl bromide [from n-octanol, conc. HBr, and conc. H_2SO_4 at 150°C for 9 h, work up and fractional distillation (b.p. 106°C/15 mm Hg) according to Vogel[26]], triphenyl trithioarsenite,[27] **4,** potassium di-O-phenylenedioxyarsenate(III),[23] **7** (**7** is difficult to obtain pure because catechol is oxidized by air very easily; **7** also contains small amounts of $KHCO_3$ and H_2O). Solvents were Analytical grade and kept over A_4 molecular sieves. TLC, using silica gel H (Merck), were run on microslides. Standards were co-run in most cases. Visualization was effected by I_2 vapors (in case the compound did not char) or by spraying with 35% H_2SO_4 and charring. Compounds containing the PhS- group give a characteristic change of colors before being charred. "Na_3AsO_3" can be detected on the plate (white spot with I_2) with R_f 0.05 in $CHCl_3$/MeOH 20:1, R_f 0.20 in $CHCl_3$/MeOH 5:1, R_f 0.67 in MeOH/conc. NH_3 4:1. As(III) was determined titrimetrically in buffered, with $NaHCO_3$, solution with standard iodine solution.[28] IR and ^{1}H-NMR

spectra were obtained on a Perkin Elmer model 16PC FT-IR and a Varian model T-60A and a Bruker model AMX (400 MHz) spectrometers using TMS and DSS as internal standards in organic and D_2O, respectively, solutions. Elemental analyses were done by C.N.R.S., Vernaison, France.

Syntheses of compounds

rac-O-Isopropylidene-3,4-dihydroxybutyl methanesulfonate, 1a

To a cold (ice-water) solution of *rac*-1,2-O-isopropylidenebutane-1,2,4-triol (2.044 g, 14 mmol) and triethylamine (2.24 ml, 16 mmol) in 20 ml dry toluene was added dropwise during 15 min a solution of 1.649 g (14.42 mmol) mesyl chloride in 5 ml dry toluene and the solution was stirred at RT for 4 h. Et_2O (50 ml) was added to precipitate $Et_3N{\cdot}HCl$, filtered and evaporated to give an oil which was percolated through 5 g silica gel H, eluting with 50 ml Et_2O, to give 2.9629 g (94%) of the product as an oil, pure by TLC (R_f 0.70 Et_2O, R_f 0.38 Et_2O/petr. ether 1/1). Found C 43.04, H 7.30 %, calcd for $C_8H_{16}O_5S$: C 42.84, H 7.19%. IR (neat) : 2988 (m), 2940 (m), 1354 (vs), 1214 (s), 1174 (vs), 1058 (s), 976 (s), 952 (s), 906 (m), 850 (m), 800 (m), 528 (s). ^{1}H-NMR ($CDCl_3$) δ : 3.85 (m, 5H, CH_2O-SO_2, O-CH_2-CH-O), 2.60 (s, 3H, CH_3SO_2), 1.60 (m, 2H, $CH_2CH_2OSO_2$), 0.95 (d, J = 3 Hz, 6H, $(CH_3)_2C$).

3,4-dihydroxybutyl methanesulfonate, 1b

To the ester **1a** (0.7490 g, 3.34 mmol) in 5 ml MeOH, 1 drop of conc. HCl was added and stirred at RT for 30 min. Evaporation and drying in vacuo gave an oil (0.6252 g, 102%). TLC in $CHCl_3$/MeOH 10:1 showed the product, R_f 0.42, contaminated with traces of 3-hydroxytetrahydrofuran,[16,25] R_f 0.67, and ^{1}H-NMR showed the presence of MeOH. The product was not stable (at RT in 3 days became pale pink). IR (neat): 3382 (broad, s), 2940 (s), 2882 (m), 1350 (s), 1198 (vs), 1172 (vs), 1076 (m), 974 (s), 534 (s). ^{1}H-NMR (D_2O) δ : 4.50 (t, J = 6 Hz, 2H, CH_2OSO_2), 3.80 (m, 3H, $HOCH_2CHOH$), 3.30 (s, MeOH impurity), 2.80 (s, 3H, CH_3SO_2), 1.95 (m, 2H, CH_2CH_2O).

rac-O-Isopropylidene-3,4-dihydroxybutyl p-dimethylaminobenzenesulfonate

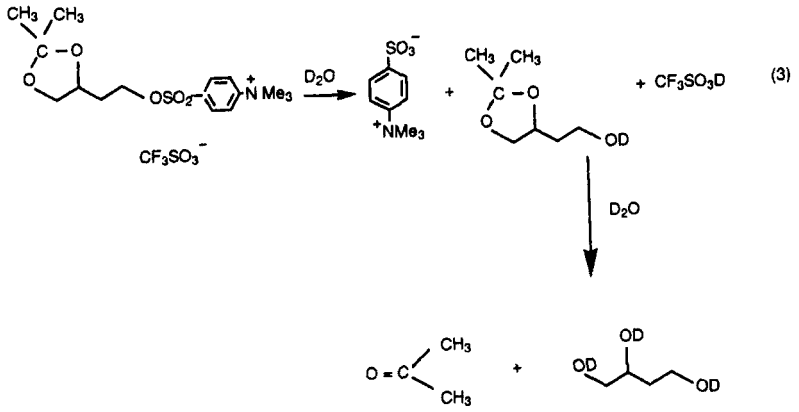
rac-1,2-O-Isopropylidenebutane-1,2,4-triol (4.5230 g, 31 mmol) was dissolved in 18 ml dry pyridine and cooled to –5°C. p-Dimethylaminobenze-

nesulfonyl chloride (6.800 g, 31 mmol) was added, the flask was swirled to dissolve the chloride (~10 min) and the solution left at +4°C for 3 days. Then was added Et_2O (150 ml), to precipitate py·HCl, and charcoal, to decolorize, and filtered through celite/silica gel H, washing with 50 ml Et_2O. Evaporation and drying in vacuo gave 9.39 g of yellowish oil which was triturated with petroleum ether. After drying in vacuo 8.73 g (86 %) of a yellow very viscous oil were obtained, pure by TLC (R_f 0.73, Et_2O). Found C 54.57, H 7.16%, calcd for $C_{15}H_{23}NO_5S$: C 54.69, H 7.04%. IR (neat): 2986 (s), 2934 (s), 1598 (vs), 1520 (s), 1352 (s), 1164 (vs), 1100 (s), 650 (s). ^{1}H-NMR (CCl_4) δ: 7.65 (d, J = 10 Hz, 2H, ortho to SO_2), 6.67 (d, J = 10 Hz, 2H, ortho to NMe_2), 4.00 (t, J = 4 Hz, 2H, CH_2OSO_2), 3.10 (s, 6H, $N(CH_3)_2$), 1.90 (m, 2H, $CH_2CH_2OSO_2$), 1.23 (d, J = 3Hz, 6H, $C(CH_3)_2$).

The esterification in CH_2Cl_2 in the presence of Et_3N and DMAP as catalyst[29] did not work.

rac-O-Isopropylidene-3,4-dihydroxybutyl p-trimethylammonium-benzenesulfonate triflate, 2d

To the *rac*-O-isopropylidene-3,4-dihydroxybutyl p-dimethylaminobenzenesulfonate (8.600 g, 26.1 mmol) dissolved in 50 ml dry benzene, methyl trifluoromethane sulfonate (3.60 ml, 31.8 mmol) was added and the yellow solution was stirred at RT for 6 h, whereupon a yellow-orange oil precipitated. The benzene was decanted, the oil washed with 20 ml dry benzene, covered with 20 ml dry petroleum ether, and cooled at −20°C overnight. The petroleum ether decanted and the solid dried in vacuo to give 12.390 g (96 %) of an off-white very hygroscopic solid. M.p. 74–6°C. The product, **2d,** is soluble in glyme, moderately soluble in H_2O, sparingly soluble in MeOH, and insoluble in benzene, petroleum ether, ether, and chloroform. It is stable at −20°C but unstable at RT (becomes brown). Found C 38.65, 39.32, 44.60, H 5.40, 5.19, 5.69%, calcd for $C_{17}H_{26}F_3NO_8S_2$: C 41.37, H 5.31%. IR (KBr): 3458 (m, due to hygroscopicity), 1496 (m), 1364 (m), 1270 (vs), 1260 (vs), 1184 (s), 1032 (vs), 942 (m), 640 (s), 570 (m). The compound was decomposed in D_2O and after 15 min peaks due to p-trimethylammoniumbenzenesulfonate[13] and acetone at 3.66 (s) and 2.20 (s) appeared according to equation (3):



2,2-Dimethylisothiazolidinium 1,1-dioxide triflate

To 1.9893 g (14.7 mmol) N-methylpropanesultam dissolved in 20 ml dry benzene, methyl trifluoromethane sulfonate (2.00 ml, 17.6 mmol) was added and the solution stirred at RT for 48 h. The benzene was decanted, the transluscent precipitate was washed with benzene and dried in vacuo to give 3.7980 g (86%) of a white microcrystalline solid, which was immediately used, as King et al.[14] suggested, for the next preparation.

n-Octyl 3-(dimethylamino)propanesulfonate

Prepared as a yellow-orange oil (containing traces of octanol by TLC) according to King et al.[14] and converted to the [3]betylate, **3a.**

3-(n-Octoxysulfonyl)-N,N,N-trimethylpropanaminium triflate, 3a

To a clear yellow solution of n-octyl 3-(dimethylamino)propanesulfonate (3.311 g, 11.5 mmol) in 20 ml dry benzene was added methyl trifluoromethane sulfonate (1.69 ml, 15 mmol). Heat was evolved but cooling was not necessary. After stirring at RT for 1 h the solvent and excess methyl triflate were evaporated, the octyl methyl ether was removed by extracting the oil with Et_2O (2 × 10 ml), and the oil was dried in vacuo to give 5.0126 g (98%) of a pale orange very viscous oil. The product, **3a,** is soluble in benzene, chloroform, water, methanol and DMF, and insoluble

in ether and petroleum ether. Found C 39.07, 39.25, H 7.30, 7.27%, calcd for $C_{15}H_{32}F_3NO_6S_2$: C 40.62, H 7.27%. IR (neat): 2928 (s), 2858 (s), 1482 (s), 1358 (s), 1260 (s), 1226 (s), 1164 (s), 1032 (s), 946 (s), 640 (s), 576 (s), 518 (s). ^{1}H-NMR ($CDCl_3$) δ : 4.25 (t, J=6 Hz, 2H, CH_2O), 3.60 (m, 2H, CH_2N), 3.25 (s, 9H, NMe_3), 2.95 (m, 2H, $CH_2CH_2CH_2N$), 2.35 (m, 2H, OSO_2CH_2), 1.75 (m, 2H, CH_2CH_2O), 1.30 (s, 10H, $(CH_2)_5$), 0.82 (m, 3H, CH_3).

1-Pinacoloxy-1-arsa-2,5-dioxa-3-dimethyl-4-dimethyl-cyclopentane, 6

Anhydrous pinacol (1.1920 g, 10.1 mmol) and As_2O_3 (0.4988 g, 2.52 mmol) were heated at 130°C with gentle stirring, in a fume cupboard, for 6 h, and then at 150°C for 4 h. After cooling at RT the solid was dissolved in minimum amount of CH_2Cl_2 (~3 ml), pentane (~30 ml) was added and cooled at −20°C overnight. The supernatant was decanted and the solid dried in vacuo to give 0.8260 g (53%) of a white solid. M.p. 108–110°C (lit.[22] 110°C). The ester **6** is soluble in Me_2CO, CH_2Cl_2, $CHCl_3$, AcOEt, DMF, DMSO, pyridine, MeOH, soluble in warm MeCN, CCl_4, hexane, sparingly soluble in H_2O. Found As 24.45%, calcd for $C_{12}H_{25}O_4As$: As 24.35%. IR (KBr): 3380 (broad, s), 2980 (s), 2950 (s), 1470 (m), 1450 (m), 1390 (m), 1375 (vs), 1370 (vs), 1170 (vs), 1150 (vs), 970 (s), 945 (s), 880 (vs), 840 (s), 830 (s), 740 (s), 700 (s), 665 (s), 640 (s). ^{1}H-NMR ($CDCl_3$) 2.90 (s, 1H, -OH), 1.35 (s, 12H, chelated pinacol), 1.25 (s, 12H, non-chelated pinacol).

Reactions of Na_3AsO_3 with various electrophiles

Na_3AsO_3 solutions were freshly prepared by dissolving 49.5 mg (0.25 mmol) As_2O_3 in 0.115 ml 13 M NaOH with slight warming in a 5 ml round bottom flask. Then, the electrophile (0.5 mmol) was added (neat or in a solvent) stirred (at RT or higher), and worked up or analysed by TLC and titrimetrically with standard iodine solution.

a) With 1b

After 30 min stirring at RT, TLC showed no starting ester, **1b,** no arsonic acid[16] but the presence of butane-1,3,4-triol (R_f 0.78, MeOH/conc. NH_3 4:1). Titration gave 45.7 mg As_2O_3.

b)With 1a

After stirring at 60°C for 7 h and at 25°C for 3 days TLC (Et_2O) showed the ester **1a** and *rac*-1,2-O-isopropylidenebutane-1,2,4-triol (R_f 0.24, Et_2O). Titration gave 0.486 mmol As(III). When the reaction was run in the presence of 20 or 40% NaI as catalyst, under the same as above conditions, titrations gave 0.488 and 0.482 mmol As(III). TLC (Et_2O) showed unreacted **1a,** *rac*-1,2-O-isopropylidenebutane-1,2,4-triol and traces of isopropylidene ketal of *rac*-3,4-dihydroxybutyl iodide (R_f 1.00, Et_2O; 0.84, Et_2O/petr. ether 1:1).

c)With amsylates 2 and [3]betylate 3a

The electrophiles **2a-2d, 3a** were added neat or in a solvent (H_2O, Et_2O, C_6H_6 or DMSO) and stirred at various temperatures (RT to 140°C) for 10–45 min. Smell of butanols and octanol was evident, TLC revealed the presence of non-volatile alcohols, Na_3AsO_3, p-trimethylammoniumbenzenesulfonate[13] (R_f 0.38, MeOH/conc. NH_3 4:1) and titrations showed no consumption of As(III). Reaction of **3a** in the presence of NaI, as catalyst, likewise gave no arsonic acid. Octanol (R_f 0.77, Et_2O) and octyl iodide (R_f 1.00, Et_2O) were detected by TLC. **3a** did not react at all in a two-phase system (H_2O/C_6H_6) after 3 days stirring at RT.

Reaction of $(PhS)_3As$, 4, with 2c

a)Without catalyst

To 201 mg (0.5 mmol) triphenyl trithioarsenite, **4,** dissolved in 1 ml dry CH_2Cl_2 was added 238.6 mg (0.5 mmol) ester **2c** and stirred at RT for 3 days. After 30 min a white microcrystalline solid started precipitating. Centrifugation gave 52.7 mg of a solid which by titration was As_2O_3 (expected 49.5 mg), and a supernatant which was evaporated and extracted with petroleum ether to give 159 mg diphenyl disulfide [m.p. 57°C (lit.[30] 61–2°C); TLC: R_f 0.46, petr. ether], and 234 mg of a solid which was the starting ester, **2c** (by m.p. and TLC).

b)With $AlCl_3$ catalyst

To a solution of 197.3 mg (0.49 mmol) **4** and 234 mg (0.49 mmol) **2c** in 2 ml dry benzene, $AlCl_3$ (196 mg, 1.47 mmol) was added (heat evolved) and the system stirred at RT for 45 min. The benzene was evaporated and the solid (0.7386 g) treated with 3 ml of 95% EtOH for 1 h and centri-

fuged. The supernatant gave a gum which was $Al(OH)_3$ and an oil which was identified as octyl phenyl sulfide (by ^{1}H-NMR) (TLC : R_f 0.72, petr. ether) contaminated by another two unknown compounds (TLC : R_f 0.50 and 0.87, petr. ether). The crude yield of the sulfide was 67%. The precipitate was worked up to give $(PhS)_3As$ (60%) (identified by m.p., TLC and ^{1}H-NMR), and p-trimethylammoniumbenzenesulfonate[13] (85%) [identified by TLC, ^{1}H-NMR, and m.p.]. Thus 82% of the PhS- groups in **4** have been recovered.

Reaction of As_2O_3 with $BF_3{\cdot}Et_2O$

To 49.5 mg (0.25 mmol) As_2O_3 in 2 ml dry Et_2O (or in 2 ml dry benzene), $BF_3{\cdot}Et_2O$ (0.09 ml, 0.75 mmol) was added and the system stirred at RT for 24 h. The crystals of As_2O_3 slowly gave a bulkier white solid. Evaporation and drying in vacuo gave 47.5 mg As_2O_3.

Reaction of 2c with $BF_3{\cdot}Et_2O$

To the ester **2c** (70 mg, 0.147 mmol) suspended in 0.7 ml dry Et_2O was added $BF_3{\cdot}Et_2O$ (0.15 ml, 1.17 mmol) and stirred at RT for 24 h. Evaporation and drying in vacuo gave 105 mg of a brownish oil, corresponding to **2c**·3.5BF_3. The oil was treated with 1 ml of 95% EtOH for 1 h and centrifuged. The precipitate was recrystallized from water to give 24 mg of needles, m.p. 124–6°C which was identified by IR (peak at 1302 due to B-O stretching, absent from **2c**) and ^{1}H-NMR (singlet at δ 1.57, disappearing by adding D_2O) as the borate salt of octyl betylate. IR (KBr): 3340 (broad, s), 2926 (s), 1484 (m), 1474 (m), 1366 (s), 1302 (w), 1184 (s), 1122 (s), 1084 (s), 1030 (s), 948 (s), 848 (s), 640 (m), 584 (m), 570 (m). ^{1}H-NMR ($CDCl_3$) δ: 8.00 (m, 4H, Ph), 4.05 (t, J = 6.6 Hz, 2H, CH_2O), 3.59 (s, 6H, NMe_3), 1.62 (quintet, 2H, CH_2CH_2O), 1.57 (s, 2H, $H_2BO_3^-$), 1.21 (m, 10H, $(CH_2)_5$), 0.79 (t, J = 7 Hz, 3H, CH_3).

Reaction of As_2O_3 with 2c

To 49.5 mg (0.25 mmol) As_2O_3 in 2 ml dry Et_2O was added $BF_3{\cdot}Et_2O$ (0.22 ml, 1.75 mmol) and stirred at RT for 1 h. Then **2c** (238.5 mg, 0.5 mmol) was added and the system stirred at RT for 3 days. The Et_2O was removed, 3 ml of 95% EtOH was added, stirred at RT for 1 h, and centri-

fuged. The precipitate contained 0.29 mmol As(III) and the borate salt of octyl betylate. The supernatant contained 0.19 mmol As(III) and **2c.**

Reactions of 7 with 2c and 3a

The ester **2c** (119 mg, 0.25 mmol) was dissolved in 2 ml dry benzene, the solution boiled to expel O_2, the complex **7** (82.5 mg, 0.25 mmol) was added and the system stirred at 50°C for 12 h and at RT for 12 h. Centrifugation gave a precipitate (149 mg) containing p-trimethylammoniumbenzenesulfonate (by TLC), the salt CF_3SO_3K, and polymerized (?) catechol. The supernatant was treated with water (a few drops), evaporated and dried to give 58 mg of an oil which contained ~5% octanol (TLC: R_f 0.24, Et_2O/petr. ether 1:3) and a product (TLC: R_f 0.83, Et_2O/petr. ether 1:3) which was identified as monooctyl ether of catechol, **8,** by ^{1}H-NMR. ^{1}H-NMR ($CDCl_3$) δ: 6.80 (s, 4H, Ar), 5.20 (broad s, 1H, -OH), 3.95 (t, J = 7 Hz, 2H, ArOCH_2), 1.95 (broad s, 2H, ArOCH$_2CH_2$), 1.35 (s, 10H, $(CH_2)_5$), 0.87 (m, 3H, CH_3).

The same results were obtained from the reaction of **7** with **3a.** The As(III) cannot be measured titrimetrically with I_2 since I_2 oxidizes the catechol.

Reaction of 7 with RBr

Under the same conditions as above, we obtained a yellow-orange oil which by TLC, IR and ^{1}H-NMR was octyl bromide (92% recovery) contaminated with traces of octanol. No reaction was observed when other solvents (DMF, DMSO, octyl bromide) were used at 50–90°C for 1–4 days.

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