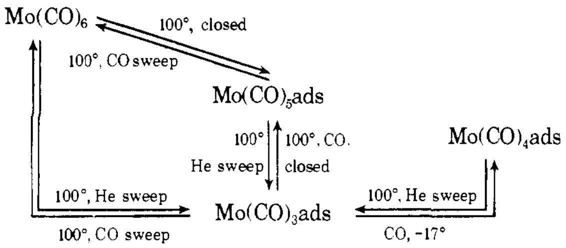

Figure 1.

gree of removal was nearly attained in 30 min. Mo(CO)$_5$ads reacts similarly.

Thus, at 100°, Mo(CO)$_6$/Al$_2$O$_3$ decomposes to Mo(CO)$_5$ads which further decomposes to Mo(CO)$_3$ads. The second step is favored by low P_{CO} and prevented by P_{CO} greater than 0.07 atm. Mo(CO)$_x$ads can be nearly completely reconverted to Mo(CO)$_6$ + γ-Al$_2$O$_3$ by sweeping with carbon monoxide at 100°. The activity[5] of both fresh and used Mo(CO)$_3$ads catalysts swept with carbon monoxide at 100° declined approximately in proportion to the amount of molybdenum removed.

Of course, the decomposition of nickel tetracarbonyl to metallic nickel has long been known to be reversible. The reactions of this communication may be more closely related to the observations of Watters[6] that treatment with oxygen eliminates the carbonyl bands in the infrared from Rh$_6$(CO)$_{16}$ deposited on alumina, and that exposure to carbon monoxide regenerates Rh$_6$(CO)$_{16}$. Here, bulk metal appears not to be formed. The new feature of the work of this communication is the reversible formation of intermediate surface carbonyl species.

$$Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4CO(g)$$

References and Notes

[1] R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Dev.*, **3**, 170 (1964).

[2] (a) E. S. Davie, D. A. Whan, and C. Kemball, *J. Chem. Soc. D*, 1430 (1969); (b) *J. Catal.*, **24**, 272 (1972); (c) R. F. Howe, D. E. Davidson, and D. A. Whan, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2266 (1972).

[3] R. L. Burwell, Jr., and A. Brenner, Proceedings of the International Conference on Relations between Heterogeneous and Homogeneous Catalytic Phenomena, Brussels, Oct 23–25, 1974, in press.

[4] The procedure just described will have led to about 60% dehydroxylation of the surface of alumina [J. B. Peri, *J. Phys. Chem.*, **69**, 211 (1965)], i.e., to a surface containing roughly equal amounts of surface OH$^-$ and O^{2-}. Use of alumina with much lower or higher degrees of dehydroxylation gives results which differ in some details from the results of this paper.

[5] Propylene pulses (0.86 cm^3 STP) were passed over samples of Mo(CO)$_3$ads in a helium flow of 1 cm^3 per sec at 53°. The conversion to propylene was roughly 2% with greater than 99.8% selectivity to ethylene and 2-butenes.

[6] G. C. Smith, T. P. Chojnacki, K. Iwatate, and K. L. Watters, *Inorg. Chem.*, **14**, (1975), in press.

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Quaternary Methylsulfonylammonium Salts. New Reagents for Mesylation. The Mechanism of Hydrogen Multiexchange in Sulfene Reactions

Sir:

We recently reported[1] that trimethylamine and other unhindered tertiary amines react with methanesulfonyl chloride (**1**) in the presence of excess D$_2$O to give mainly CD$_3$SO$_3^-$ and suggested that this multiexchange points to the occurrence of the following reactions.

$$\underset{\mathbf{1}}{CH_3SO_2Cl} \xrightarrow{R_3N} \underset{\mathbf{2}}{CH_2{=}SO_2} \overset{R_3N}{\rightleftharpoons} \underset{\mathbf{3}}{\bar{C}H_2{-}SO_2\overset{+}{N}R_3} \overset{H^+X^-}{\rightleftharpoons} \underset{\mathbf{4}}{CH_3SO_2\overset{+}{N}R_3X^-}$$

Such a scheme, if correct, would require that the trimethyl(methylsulfonyl)ammonium salt (**4**, R = Me) yield the multiexchanged product on similar treatment in D$_2$O. We wish to report herein the synthesis[2] of specific examples of **4** and describe experiments which (a) provide confirmation for the above scheme and (b) show such quaternary methylsulfonylammonium salts (**4**) to be valuable reagents for forming methanesulfonate (mesylate) esters and related species.

Reaction of **5a–d** with excess neat methyl fluorosulfonate under the specified reaction conditions gave the following methylsulfonylammonium fluorosulfonates:[4] **6a**, mp ~130° dec (after *1* hr at 20°, *85%*); **6b**, mp ~*120*° dec (after *18* hr at 60°, 81%); **6c**, mp ~100° dec (after 16 days at 25°, 28%); **6d**, mp ~115° dec (after 72 hr at 50°, 64%). The crystalline salts are (a) attacked by moist air but may be kept for extended periods (at least 6 months) in sealed ampoules and (b) soluble in acetonitrile, the solutions gradually decomposing in a few hours at room temperature.

$$\underset{\mathbf{5}}{MeSO_2NRR'} + MeOSO_2F \longrightarrow \underset{\mathbf{6}}{MeSO_2\overset{+}{N}MeRR'FSO_3^-}$$

a, R,R′ = Me
b, RR′ = $-(CH_2)_5-$
c, R = Me; R′ = Et
d, R,R′ = Et

The NMR spectra, in conjunction with elemental analyses and the formation of the corresponding tertiary amine on hydrolysis, show the methylation to have occurred on nitrogen rather than on oxygen.[5] When R and R′ in **5** were larger than ethyl (e.g., isopropyl or butyl) no reaction was observed at room temperature, and on heating only extensive decomposition was observed.

Reaction of **6a** with D$_2$O in 1,2-dimethoxyethane in the presence of the trimethylamine gave methanesulfonate anion of the following composition: CD$_3$SO$_3^-$, 64.2; CHD$_2$SO$_3^-$, 29.2; CH$_2$DSO$_3^-$, 5.3; CH$_3$SO$_3^-$, 1.3%.[6] The extent of multiexchange decreased progressively from **6a** to **6d**, in full accord with previous results[1] and with the above scheme. With D$_2$O and pyridine **6a, 6b,** and **6d** give almost complete multiexchange (>80% CD$_3$SO$_3^-$, >90 atom % D).

These methylsulfonylammonium salts react under very mild conditions with amines and alcohols to give the corresponding methanesulfonamides or mesylate esters in high yield. For example, reaction of **6a, 6b,** or **6d** with *p*-toluidine gives the *p*-toluidide quantitatively in 5 min at 25°, and with 5α-cholestan-3β-ol plus a *catalytic* amount of pyridine or *N,N*-dimethylaminoacetonitrile (DMAA) the corresponding mesylate ester was isolated in >90% yield after 30 sec at 0°. Even at −70° **6d**[7] and pyridine quickly gave cyclohexyl mesylate from cyclohexanol in high yield. With *tert*-butyl alcohol, bands at 1.57 and 3.03 ppm assigned to *tert*-butyl mesylate (and none appropriate to *t*-BuOH) were observed when *t*-BuOH (0.25 mmol), **6d** (0.5 mmol), and pyridine (10 ml) were mixed at −5° in CD$_2$Cl$_2$–CD$_3$CN. On warming to room temperature, these peaks were replaced by the characteristic bands of isobutene; attempts to isolate the ester were unsuccessful.

With borneol, presumably for steric reasons, yields of the mesylate with the different sulfonylammonium salts (**6**)

Table I. Formation[a] of Mesylate Esters with "Easy Mesyl"[7] (**6d**)

Alcohol	% conversion of alcohol With 1.2 equiv of **6d**	 With 2.0 equiv of **6d**
Ethanol[b]	64	98
Cyclohexanol	83	98
Menthol	100	*c*
1-Octanol	82	100
Borneol	89[d,e]	*c*
5α-Cholestan-3β-ol	100	*c*
5α-Cholestan-3α-ol	~80	84[f]
Phenol	100	*c*
Allyl alcohol	75	92
Benzyl alcohol	85	100

[a] For reaction conditions, see text. [b] In the absence of base there is only very slow reaction. [c] Not tried. [d] Bornyl "mesylmesylate" (11%) also formed; see text. [e] With 1.5 equiv **6d** used. [f] The "mesylmesylate" (14%) also formed; see text.

were variable; this made it possible to determine some of the factors which lead to optimal yields. The best yield (89%) was obtained with **6d** using a catalytic amount of DMAA; with **6a** or **6b** with DMAA or pyridine the yields of bornyl mesylate were as high as 30-50%, whereas with stronger bases (e.g., triethylamine) yields of the mesylate were negligible with **6a, 6b,** or **6d.** Table I shows the results of experiments using **6d** in a standard procedure (addition of a solution of **6d** in CH_3CN at 0° to a solution of 1 mmol of the alcohol and 0.1 mmol of DMAA in CH_2Cl_2 at 0°, and letting the mixture stand at 0° for 10 min). The yields given are estimated from the weight and NMR spectra of the products following conventional extraction and washing; except where otherwise indicated the products were evidently substantially pure (>95%). This mode of reporting the yield was necessitated by the instability of some of these esters, since the yield of the product after further purification would give little information about the efficiency of the esterification itself.

In addition to the mesylate, another product, viz, the "mesylmesylate" ($CH_3SO_2CH_2SO_2OR$), was also formed in the reactions with the less reactive alcohols, e.g., borneol. A mesylmesyl derivative can also be formed in other ways, e.g., when **6a** is mixed with trimethylamine and *p*-toluidine added 30 sec later, or with **6a** and *p*-toluidine with triethylamine. The mesylmesyl products very likely arise from the stabilized zwitterion[8] $CH_3SO_2^-CHSO_2NR_3^+$ (**7**), formed via the sequence **2** + **3** → $[^-CH_2SO_2CH_2SO_2NR_3^+]$ → **7.** Formation of mesylmesyl derivatives relative to mesylates are thus predicted—and found—to be minimized by (a) the presence of reactive sulfene traps and (b) factors favoring a low concentration of **3**, e.g., (i) having the R groups in **3** relatively large, (ii) using a weak base, and (iii) minimizing the concentration of NR_3.

Because the quaternary methylsulfonylammonium salts (a) require only a catalytic (rather than stoichiometric) quantity of base and (b) react quickly and in high yield, even at low temperatures, these species appear to us to be the reagents of choice for many mesylations, especially those leading to highly sensitive mesylate esters. Experiments designed to explore the selectivity of these reagents are now in progress.

"Easy Mesyl" (**6d**) was prepared as follows. *N,N*-Diethylmethanesulfonamide (10 g) was dissolved in methyl fluorosulfonate (Aldrich, "Magic Methyl") (20 ml) in a two-necked, round-bottomed flask equipped with an inlet tube for dry nitrogen and a condenser fitted with a drying tube of indicating silica gel. The contents of the flask were heated to 50° for 3 days under dry nitrogen, then diluted with dry methylene chloride (50 ml) and cooled in a Dry Ice-acetone bath. When crystallization appeared complete, the diethylmethylammonium salt was collected and washed with dry methylene chloride in a drybox under nitrogen, yield 11.15 g (64%), mp ~115 dec. The product was used for reactions without further purification. The NMR spectrum showed (CD_3CN): δ 1.40 (6 H, triplet, $J = 7$ Hz), 3.11 (3 H, singlet), 3.60 (4 H, quartet, $J = 7$ Hz), and 3.70 (3 H, singlet). An analytical sample was recrystallized from acetonitrile-methylene chloride solution at −78°.[9]

Supplementary Material Available. Further experimental details will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, Americal Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2566.

References and Notes

(1) J. F. King, E. A. Luinstra, and D. R. K. Harding, *J. Chem. Soc., Chem. Commun.* 1313 (1972).

(2) Trialkyl(*aryl*sulfonyl)ammonium salts were first described many years ago,[3] but to the best of our knowledge credit for the first preparation of a quaternary *alkyl*sulfonylammonium salt belongs to R. W. Alder and M. H. Ahmed (University of Bristol), who found that **5a** and methyl fluorosulfonate give a crystalline product which was assigned structure **6a** on the basis of its NMR spectrum. We learned of this experiment before beginning our work from Professor M. C. Whiting (with further data provided subsequently by Dr. Alder); we thank Professor Whiting and Dr. Alder most cordially for this invaluable information.

(3) (a) D. Vorländer and M. Kauffmann, *Ber.*, **43**, 2735 (1910); cf. L. Horner and H. Nickel, *Justus Liebigs, Ann. Chem.*, **597**, 20 (1955) and also C. R. Gambill, T. D. Roberts, and H. Shechter, *J. Chem. Educ.*, **49**, 287 (1972), and references cited; (b) T. Oishi, K. Kamata, and Y. Ban, *Chem. Commun.*, 777 (1970).

(4) Compounds **6a** and **6b** crystallize from the reaction mixture, the first while the reaction proceeds, the second upon subsequent cooling. With **6c** and **6d** the crystalline product was obtained after addition of CH_2Cl_2 and cooling to −70°. The salts were recrystallized for analysis from $CH_3CN-CH_2Cl_2$.

(5) Cf. G. R. Chalkley, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc. C*, 682 (1970).

(6) The reaction conditions and analysis were as previously described.[1]

(7) The systematic name for **6d**, diethylmethyl(methylsulfonyl)ammonium fluorosulfonate, is sufficiently inconvenient to prompt us to offer something shorter. Our personal choice is "Easy Mesyl", but for those who prefer the sobriety of an acronym we offer (rather half-heartedly) "DEMMSAF" or perhaps "DEMMSA$^+$ FSO_3^-".

(8) G. Opitz, M. Kleeman, D. Bücher, G. Walz, and K. Rieth, *Angew. Chem., Int. Ed. Engl.*, **5** 594 (1966); G. Opitz and D. Bücher, *Tetrahedron Lett.*, 5263 (1966); J. S. Grossert and M. M. Bharadwaj, *J. Chem. Soc., Chem. Commun.*, 144 (1974).

(9) Further experimental details regarding the preparation and use of these reagents appear in the microfilm edition. See paragraph at end of paper regarding supplementary material.

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Asymmetric Hydrogenation with a Complex of Rhodium and a Chiral Bisphosphine

Sir:

We have previously reported asymmetric hydrogenations[1] with efficiencies of 85-90% using a rhodium-chiral *o*-anisylcyclohexylmethylphosphine complex.[1e] In this update, we wish to report further improvements in the selectivity of these catalysts. Enantiomeric excesses of 95-96% were achieved in the reduction of α-acylamidoacrylic acids using a chiral bisphosphine[2] [1,2-bis(*o*-anisylphenylphosphino)ethane], **3,** as a ligand. The resulting amino acid intermediates have thus been prepared by a synthetic route which rivals the stereospecificity observed with enzymes. The bisphosphine was made by the sequence shown in Scheme I. Oxidative coupling of *o*-anisylmethylphenylphos-