163°; authentic sample 162.5-164.[30] Since **12** can be debenzylidenated and converted to sucrose **13** or its octaacetate **14**, the foregoing constitutes a total synthesis of sucrose.

The promise of dienoid receptors for the synthesis of divers α-linked di- and oligosaccharides is apparent from the results in Scheme 2 where a range of alcohols and the yields obtained are reported. Notably only α-D anomers have been observed. Sample syntheses designed to develop this approach are underway and will be reported in due course.

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(31) Holder of a National Research Council of Canada Studentship, 1973-1975.

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Reversibility in the Formation of Stoichiometric Surface Molybdenum Carbonyls on Alumina

Sir:

Suitable activation converts molybdenum hexacarbonyl adsorbed on γ-Al_2O_3 into a catalyst for the metathesis of olefins at low temperatures.[1,2] Sweeping $Mo(CO)_6/\gamma$-Al_2O_3 with a flow of ultrapure helium at 100° results in the loss of carbon monoxide and the formation of a material with catalytic activity and an empirical composition of $Mo(CO)_3$ads. Preliminary data indicated that decomposition terminated very approximately at $Mo(CO)_5$ads when the treatment was in a closed vessel with resulting development of a partial pressure of carbon monoxide, and that exposure of $Mo(CO)_3$ads to carbon monoxide at −17° converted it to $Mo(CO)_4$ads.[3] Further data support the existence of this novel group of stoichiometric surface compounds and establish that the formation of these compounds can be reversed to molybdenum hexacarbonyl plus γ-Al_2O_3 by appropriate treatment with carbon monoxide with proportional loss in catalytic activity. Our data are summarized in Figure 1.

$Mo(CO)_3$ads was prepared by cleaning 0.250 g of 60-80 mesh γ-Al_2O_3 (Harshaw Chemical Co. AL3940, prepared from Catapal SB) in flowing oxygen at 450°, cooling in helium, impregnating at 0° with a pentane solution of $Mo(CO)_6$ (to provide about 15 mg $Mo(CO)_6$/g Al_2O_3 in most experiments), evaporating the pentane in a flow of helium at 0°, and then activating for 1 hr at 100° in a flow of helium. The evolved carbon monoxide was trapped at −196° on wide pore silica gel (Davison grade 62) and later released by warming for catharometric measurement.[3,4] In these experiments, 3.00 ± 0.03 CO/Mo were released. In the absence of alumina, decomposition is very slow at 100°.

A helium sweep of the reactor after heating $Mo(CO)_6/Al_2O_3$ in a closed system at 100° for 1 hr followed by cooling to 0° collected 1.02 CO/Mo. The P_{CO} at the end of the activation at 100° was about 0.07 atm.

A reactor containing $Mo(CO)_3$ads was exposed to 1 atm of carbon monoxide for 30 min at 100°, cooled to −17° evacuated, and purged with helium for 15 min. Reconversion of the resulting material to $Mo(CO)_3$ads by a helium sweep at 100° for 50 min liberated 2.12 ± 0.14 CO/Mo (three experiments).

During the passage of several pulses of carbon monoxide in a helium carrier over $Mo(CO)_3$ads at −16°, 1.06 CO/Mo disappeared. In seven other experiments, $Mo(CO)_3$ads was exposed to P_{CO} = 1 atm at −17° for 15 min, the system was evacuated and then swept with helium for 15 min. Sweeping the product with helium at 100° for 40 min released 1.04 ± 0.08 CO/Mo.

A flow of carbon monoxide at 100° passed over $Mo(CO)_3$ads (either freshly prepared or after use as a catalyst for the disproportionation of propylene) results in the removal of about 90% of the original $Mo(CO)_3$ads as molybdenum hexacarbonyl collected in a trap at −78°. This de-

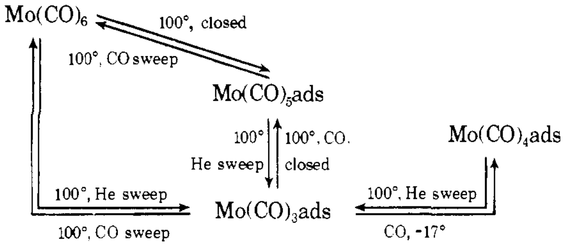

Figure 1.

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

Thus, at 100°, $Mo(CO)_6/Al_2O_3$ 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 $Mo(CO)_6 + \gamma\text{-}Al_2O_3$ 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.

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

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(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.

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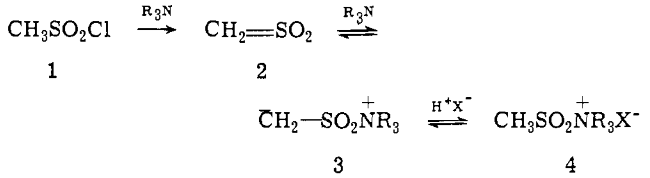
Quaternary Methylsulfonylammonium Salts. New Reagents for Mesylation. The Mechanism of Hydrogen Multiexchange in Sulfene Reactions

Sir:

We recently reported[1] that trimethylamine and other unhindered tertiary amines react with methanesulfonyl chloride (**1**) in the presence of excess D_2O to give mainly $CD_3SO_3^-$ 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_2O. 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_2O in 1,2-dimethoxyethane in the presence of the trimethylamine gave methanesulfonate anion of the following composition: $CD_3SO_3^-$, 64.2; $CHD_2SO_3^-$, 29.2; $CH_2DSO_3^-$, 5.3; $CH_3SO_3^-$, 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_2O and pyridine **6a, 6b,** and **6d** give almost complete multiexchange (>80% $CD_3SO_3^-$, >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_2Cl_2–CD_3CN. 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**)