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(11) Fluorescence lifetimes were determined by R. Brewer in the laboratory of M. F. Nicol at UCLA. Values of τ_s in both CH_3CN and CD_3CN were the same within experimental error. The apparatus used has been described in detail elsewhere.[12] For the MB determination, λ_{exc} was 620 nm, λ_{em} 677 nm. Saturation of the samples with air had no measurable effect on the fluorescence lifetime.

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A New, Convenient, and Efficient Route to Dimolybdenum(II) Compounds from MoO_3

Sir:

Since the discovery and recognition of quadruple bonds between metal atoms,[1] hundreds of compounds containing $M \equiv M$ (M = Cr, Mo, W, Tc, Re) were prepared. Molybdenum has been the subject of the greatest and still growing number of reports about these compounds.[2] The interest in the $[Mo \equiv Mo]^{4+}$ unit and its derivatives stems firstly from the quadruple bonds themselves and secondly from their use as reactants in the preparation of many other interesting molybdenum compounds.[2] Nevertheless, this part of the molybdenum chemistry has been considered by many chemists as an exotic field, separated from the conventional chemistry of this element. The origin of this erroneous concept was the fact that, until now, there has not been any report of a simple synthetic procedure which describes the forming of the unit $[Mo \equiv Mo]^{4+}$ by reduction of molybdenum species of higher oxidation number. Almost all of the procedures which have been used involve the relatively expensive starting material, $Mo(CO)_6$.[3]

All these reactions are carried out under severe anhydrous and anaerobic conditions and do not always produce high yields of $Mo_2{}^{4+}$.

Attempts to reduce Mo(VI) in aqueous media by strong reducing agents invariably yielded only Mo(III) species which could not be reduced any further by any conventional method.

This report shows, for the first time, a simple way to convert MoO_3 into $[Mo \equiv Mo]^{4+}$ derivatives, by using conventional reduction methods in aqueous media. This synthesis consists of three steps, two of which have already been known in the literature for many years. The first step is the electrolytic reduction of Mo(VI) in HCl to $MoCl_6{}^{3-}$.[5] The second, described by Nyholm et al. in 1969,[6] was the condensation reaction of $MoCl_6{}^{3-}$ to produce the triply bridged dinuclear $Mo_2Cl_9{}^{3-}$ by evaporation of the aqueous HCl solution of $MoCl_6{}^{3-}$ to near dryness.

We report now that $Mo_2Cl_9{}^{3-}$ and $Mo_2Br_9{}^{3-}$ can be reduced quantitatively by an amalgamated zinc column (Jones reductor) to the dimolybdenum(II) $[Mo \equiv Mo]^{4+}$ species and that compounds derived from this species, such as $Mo_2(O_2CCH_3)_4$,[7] $K_4Mo_2Cl_8 \cdot 2H_2O$,[8] and $K_4Mo_2(SO_4)_4 \cdot 2H_2O$,[9] can be obtained.

MoO_3 (2 g) was dissolved in 50 mL of HCl (12 M).[5] This solution was reduced electrolytically to $MoCl_6{}^{3-}$ in a cell using a platinum cathode and a graphite rod anode separated by a porous clay compartment.[10] The red solution of $MoCl_6{}^{3-}$ was then evaporated to near dryness with a rotating evaporator, 80 mL of HCl (0.6 M) was added, and the solution was passed through an ice-cooled Jones-reductor column (15 × 1 cm) into a solution containing sodium acetate (5 g) in 30 mL of H_2O. The heavy yellow precipitate of $Mo_2(O_2CCH_3)_4$ was collected, washed with water, acetone, and ether, and dried under vacuum: yield, 2.37 g (80%). When the sodium acetate was omitted, a deep red solution of $Mo_2{}^{4+}$ was obtained from the reductor. By passing gaseous HCl into this solution at −10 °C, followed by the addition of KCl, the salt $K_4Mo_2Cl_8 \cdot 2H_2O$ was precipitated. The red compound was filtered, rinsed with alcohol and ether, and dried under vacuum: average yield, 55%. When this experimental procedure was carried out without external cooling, the temperature of the solution increased by the dissolution of the gaseous HCl, and $Mo_2Cl_8{}^{4-}$ was oxidized to $Mo_2Cl_8H^{3-}$.[11] Addition of CsCl to the resulting deep yellow solution precipitated $Cs_3Mo_2Cl_8H$: average yield, 90%. When 50 mL of H_2SO_4 (0.5 M) was added instead of HCl (0.6 M) to the almost dry $H_3Mo_2Cl_9$ and passed through the reductor into 40 mL of H_2SO_4 (2 M) containing K_2SO_4 (2 g), $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ was obtained: average yield, 60%. It was found that other Mo(III) species are reducible to $Mo_2{}^{4+}$. These species, $Mo_2X_8H^{3-}$ (X = Br, Cl)[12] and $Mo_2(HPO_4)_4{}^{2-}$ [14] do not, however, open new synthetic routes to $Mo_2{}^{4+}$ since they themselves are prepared by oxidation of $Mo_2{}^{4+}$.[11,13]

The fact that $Mo_2X_9{}^{3-}$, $Mo_2X_8H^{3-}$ (X = Cl, Br) and $Mo_2(HPO_4)_4{}^{2-}$ are reduced to $Mo_2{}^{4+}$ unlike other Mo(III) species in aqueous solution raises the question of the factors which determine the reducibility of Mo(III) species. All known molybdenum(III) species in aqueous solutions are listed in Table I, with their Mo-Mo distance and reduction behavior. The information in Table I indicates that it is essential that the starting material should have a dinuclear nature but the MoMo

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Table I. Species of Mo(III) in Aqueous Solutions

species	Mo-Mo distance, Å	reduction with Jones reductor
monomeric Mo(III)		no reduction
$[Mo_2(OH)_2]^{4+}$ [a]	2.43[b]	no reduction
$Mo_2Cl_9^{3-}$	2.65[c]	produces Mo_2^{4+} [d]
$Mo_2Br_9^{3-}$	2.82[c]	produces Mo_2^{4+} [d]
$Mo_2Cl_8H^{3-}$	2.37[e]	produces Mo_2^{4+} [d]
$Mo_2Br_8H^{3-}$	2.39[e]	produces Mo_2^{4+} [d]
$Mo_2(HPO_4)_4^{2-}$	2.23[f]	produces Mo_2^{4+} [g]

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distance is *not* a major factor in this process. In $Mo_2Br_9^{3-}$ this distance is 2.82 Å compared with 2.43 Å in $[Mo_2(OH)_2]^{4+}$; yet it is only the former that is reduced. The molybdenum to molybdenum distance is not by itself a sufficient criterion for reducibility, which is probably a combination of this distance, the geometry of the ion and the nature of the bridging ligands.

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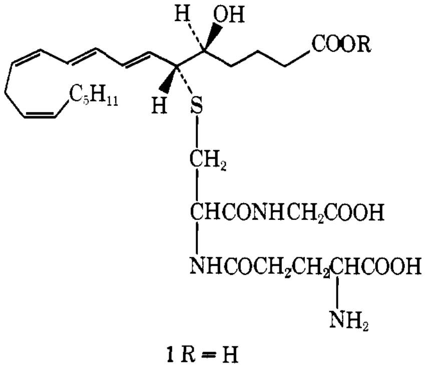
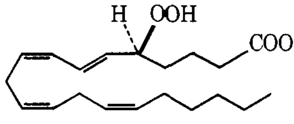
Synthesis of the Slow Reacting Substance of Anaphylaxis Leukotriene C-1 from Arachidonic Acid

Sir:

Mounting evidence implicates the class of "slow reacting substances" (SRS's) as important agonists in asthma and various forms of hypersensitivity.[1-3] A major obstacle to progress in understanding the exact role of SRS's in disease has been the lack of pure, well-defined SRS.[2] Recently this situation has been corrected by the development of an efficient total synthesis of the SRS leukotriene C-1[4] (LTC-1, **1**) and the biologically important Cys,Gly analogue of **1** (LTD) which also served to allow the assignment of chemical structure in all detail.[5] The biosynthesis of **1** is considered[5a-c] to proceed from arachidonic acid via (*S*)-5-hydroperoxy-6-*trans*,8,11,14-*cis*-eicosatetraenoic acid [(*S*)-5-HPETE] (**2**) and *trans*-5-(*S*),6-(*S*)-oxido-7,9-*trans*-11,14-*cis*-eicosatetraenoic acid (leukotriene A, **3**) as successive intermediates. In this communication we report a simple synthesis of LTC-1 (**1**) which follows the pathway of biosynthesis from arachidonic acid.



1 R = H
5 R = CH_3



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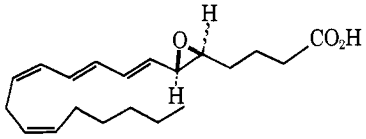

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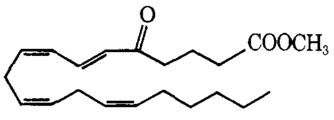

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Recently an efficient chemical synthesis of (±)-5-HPETE and an enzymic synthesis of (*S*)-5-HPETE (**2**) from arachidonic acid have been reported.[6] Both (±)-5-HPETE and (*S*)-5-HPETE can be utilized for the synthesis of LTC-1 (**1**) by conversion into **3** and subsequent combination with glutathione (natural form). The former has the advantage of being readily available in quantity, but the disadvantage of requiring separation of diastereoisomers of **1** in the final step. A description of the synthesis of **1** from (*S*)-5-HPETE is given here.

The chemical conversion of **2** into **3** (as methyl esters) requires activation of the hydroperoxy group to generate electrophilic oxygen at C-5 under *nonacidic* and mild conditions since the epoxy tetraene **3** is known to be an exceedingly labile substance, e.g., to water and other protic media, mild acids, oxygen, or free radicals. Considerable experimentation was required to achieve the desired results. Not unexpectedly, one troublesome side reaction was formation of dienone **4** by a carbonyl-forming 1,2-elimination process, and another was formation of relatively polar materials, some of which probably originate from the desired product, **3** methyl ester. Methylene chloride (or mixtures with some ether) was found to be the most satisfactory solvent (superior to chloroform, ether, tetrahydrofuran, or acetonitrile, for example). Both the degree of stabilization of the leaving group and low temperature seemed to favor the generation of desired product over the dienone **4**. Finally, it was critical not only that a proton acceptor be present to minimize the destruction of **3** methyl ester, but also that the acceptor be highly hindered to disfavor carbonyl-forming 1,2 elimination. All of these factors had to be

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