Hz,<sup>5</sup> derived by coupling to a vinylic proton  $H_C$  which was situated on an E disubstituted double bond ( $J_{\rm CD}$  = 15.2 Hz). The other proton on this E double bond (H<sub>D</sub>) was coupled to a proton on a saturated carbon (H<sub>E</sub>,  $\delta$  4.47,  $J_{DE}$ = 8.5 Hz), and a long range coupling of  $\sim$ 1 Hz between H<sub>E</sub> and  $H_C$  collapsed during spin decoupling at  $H_E$ .

These J's and decoupling experiments (Table I) are suggestive of a rather rigid carbon framework containing the protons  $H_A$ ,  $H_B$ ,  $H_C$ ,  $H_D$ , and  $H_E$  on carbons as sequenced in structure 1, and in addition a planar transoid conformation between conjugated sets of trigonal C's provides a favorable "W" path for the long range  ${}^{4}J_{\rm BC}$  = 2 Hz.<sup>6</sup> The stereochemistry about the remaining double bond is suggested to be E by comparison of the observed chemical shift for  $H_A$  ( $\delta$  7.05) vs. that calculated from tables of substituent shielding constants<sup>7</sup> giving  $H_A$  (calculated): Z isomer,  $\delta$  7.44; E isomer,  $\delta$  7.03.

Marine algae, especially of the genus Laurencia, have been observed to be a rich lode of brominated sesquiterpenes,<sup>8</sup> even though the marine environment has  $\sim 10^2$ times as much chloride vs. bromide.<sup>9</sup> Recently, however, a growing list of sesquiterpenes containing both Br and Cl within a spiro[5.5]undecane skeleton have been isolated from Laurencia.  $^{1a,g,10-12}$  In this context cartilagineal (1) is quite unique because almost no halogenated monoterpenes have been reported from marine algal sources. In addition, this compound represents, to our knowledge, the first terpenoid from marine sources containing multiple halogens bonded to carbon all of which are chlorine.<sup>13</sup> Structurally, this aldehyde bears an intriguing resemblance to the tribromotrichloro monoterpene 2 isolated from the sea hare Aplysia californica,<sup>14</sup> and also observed to be a component of p. coccineum collected in Southern California.<sup>15</sup>

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## A Novel Method for the Oxidation of Primary and Secondary Alcohols to Carbonyl Compounds

Summary: a solution of sodium dichromate and sulfuric acid in dimethyl sulfoxide oxidizes primary alcohols to aldehydes and secondary alcohols to ketones; in these oxidations DMSO acts as a solvent and not as a reactant.

Sir: Recently, there has been a host of new methods reported for the oxidation of alcohols to aldehydes and ketones. The reagents employed are DMSO-p-toluenesulfonyl chloride and methanesulfonic anhydride,<sup>1</sup> DMSO-DCC,<sup>2</sup> DMSO-SO<sub>3</sub>,<sup>3</sup> DMSO-acetic anhydride,<sup>4</sup> DMSO-P<sub>2</sub>O<sub>5</sub>,<sup>5</sup> DMSO-chloroformate,6 boiling DMSO,7 DMSO-chlorine,8 ceric ammonium nitrate in acetic acid or acetonitrile,9 Nchlorosuccinimide and dimethyl sulfide,10 chromium trioxide in pyridine<sup>11</sup> and, earlier, chromium trioxide in acetone,<sup>12</sup> activated manganese dioxide,<sup>13</sup> and aqueous sodium dichromate.14

We report here a new method for the oxidation of alcohols to aldehydes or ketones in 80-90% yields. This method is economical, efficient, and simple to operate and consists of treating a solution of sodium dichromate dihydrate in DMSO<sup>15</sup> with an alcohol and concentrated sulfuric acid. To determine the role that DMSO plays in these oxidations, we found that oxidation of benzyl alcohol with  $Na_2Cr_2O_7$ . 2H<sub>2</sub>O and sulfuric acid alone at 70° led to charring and the formation of some benzoic acid. A solution of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. 2H<sub>2</sub>O in DMSO at 70° caused only a slight oxidation of benzvl alcohol to benzaldehvde while the alcohol was recovered unchanged when heated with DMSO-H<sub>2</sub>SO<sub>4</sub>. It would appear, therefore, that DMSO acts as an excellent solvent<sup>15</sup> and prevents further oxidation of the carbonyl compound<sup>7</sup> formed and does not take part in the reaction as in other cases.<sup>2–7</sup> There was no evidence of the formation of methylthiomethyl ethers<sup>2,8</sup> of alcohols. Even if they had been formed, they would have been cleaved by the strong acid.<sup>2</sup> The unique feature of this method is that commercial DMSO may be used without further purification and the reaction takes 90 min for completion.

The following procedure represents the use of this oxidation for the preparation of an aldehyde.

Benzaldehyde. To a stirred solution of sodium dichromate dihydrate (10 g., 0.0332 mol) in 100 g of DMSO was added benzyl alcohol (5.4 g, 0.05 mol). Concentrated sulfuric acid (7.2 ml, 0.133 mol) was added dropwise, while the temperature was kept below

Communications

| Alcohol   | Product  | %<br>yield |
|---|--|------------|
| C <sub>g</sub> H <sub>5</sub> CH <sub>2</sub> OH                                    | C <sub>6</sub> H <sub>5</sub> CHO                                    | 84         |
| p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH                 | p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO                 | 87         |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> OH                  | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CHO                  | 80         |
| dl-Menthol  | dl-Menthone  | 85         |
| Cyclohexylcarbinol  | Cyclohexylcarboxaldehyde   | 80         |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> OH                    | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHO                    | 82         |
| C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> OH                    | C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> CHO                    | 90         |
| p-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> OH                | $p-C1C_6H_4CH_2CHO$  | 80         |
| p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> OH | p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CHO | 81         |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH    | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CHO    | 80         |
| C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> OH                               | C <sub>6</sub> H <sub>5</sub> CH=CHCHO                               | 85         |
| C <sub>6</sub> H <sub>5</sub> CHOHCH <sub>3</sub>                                   | C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>                      | 85         |
| C <sub>6</sub> H <sub>5</sub> CHOHC <sub>6</sub> H <sub>5</sub>                     | C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>        | 85         |
| p-ClC <sub>6</sub> H <sub>4</sub> CHOHC <sub>6</sub> H <sub>5</sub>                 | $p-\mathrm{C1C}_{6}\mathrm{H}_{4}\mathrm{COC}_{6}\mathrm{H}_{5}$     | 84         |
| Cyclohexanol  | Cyclohexanone  | 89         |

70° by occasional cooling. The mixture was heated at 70° for an additional 30 min, when it became dark green. It was poured on ice and extracted three times with 100 ml each of ether; the combined ether extract was washed once with sodium bicarbonate solution and once with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the remaining oil distilled to give 4.5 g of benzaldehyde (bp 179°), 2,4-dinitrophenylhydrazone mp 237°

This method with a slight modification is applicable to the preparation of arylacetaldehydes from 2-arylethanols which, when oxidized with ceric ammonium nitrate, give substituted benzaldehydes.<sup>16</sup> Similarly, 3-phenyl-1-propanol, 1-phenylethanol, and cinnamyl alcohol were oxidized to the corresponding carbonyl compounds in 80-85% yields. Table I contains a number of alcohols which were oxidized. All the carbonyl compounds were characterized by their boiling points (or melting points) and 2,4-dinitrophenylhydrazones.

It may be pointed out that DMSO-CrO<sub>3</sub> and DMSO- $K_2Cr_2O_7$  systems also worked in the case of benzyl alcohol. The scope of these oxidation methods to various alcohol systems is currently under investigation and will be reported later.

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## Single-Crystal Analysis of 1-Benzyl-2-phenyl-4,5-dimethylphospholan-3-one 1-Oxide. Evidence for the Enol Form 1-Benzyl-2-phenyl-3-hydroxy-4,5-dimethylphosphol-2-ene 1-Oxide

Summary: An X-ray diffraction analysis of the title compound clearly indicates the existence of the enol form and the stereochemistry at  $P \rightarrow O$  and  $CH_3$  at C(5) to be cis and the  $CH_3$  groups at C(5) and C(4) to be trans.

Sir: In a recent pmr and <sup>31</sup>Pmr study<sup>1</sup> of several substituted phospholan-3-one 1-oxides, it was strongly suggested that the oxide 1 existed to a considerable extent in the enol form 2 in  $DCCl_3$  and had the stereochemistry as illustrated.



Molecular models also favored the cis relationship of  $P \rightarrow O$ and  $CH_3$  at C(5) and trans relationship of the two  $CH_3$ groups.<sup>2-4</sup> We wish to report the first single-crystal analysis of the enol title compound, mp 181–183°.

The space group is orthorhombic  $Pc 2_1 b$  (no. 29) with unit cell dimensions of a = 8.1319 (6), b = 8.5671 (7), and c= 24.081 (3) Å for  $C_{19}H_{21}O_2P$ . The integrated intensities of 1852 independent reflections were taken on a CAD-4 automatic diffractometer, using CuK $\alpha$  ( $\lambda = 1.5418$ ) radiation. This constitutes all the independent data with  $\theta \leq 75^{\circ}$ . The structure was solved from a Patterson synthesis and the heavy atom method, and was refined by block-diagonal least-square methods. The final R value  $[R = (\Sigma || F_o| |F_{\rm c}| / \Sigma F_{\rm o}$  is 0.035.

Bond lengths and angles are given in Figure 1. The standard deviations of the P-C distances are between 0.002 and 0.003 Å. The standard deviations of the C-C distances are between 0.003 and 0.005 Å. All other results are on the figure. Figure 2 is a 3-D representation of the molecule.

First, it is apparent that the C(2)-C(3) bond is quite near that of an alkene linkage in length and that 2 is the tautomer in the solid state. Strong intermolecular H bonding is evidenced by an O-O distance of 2.593 Å between two molecules. Thus, it is strongly suggested that C(2) and C(3)are very close to sp<sup>2</sup> hybridized. This can be deduced from the observation that the sum of the three bond angles around the atoms is 360.0 and 359.9°, respectively. There is, however, a small rotation around the C(2)-C(3) bond as indicated by the conformational angle of 8° for the atoms PC(2)C(3)C(4). This probably is correlated with the obser-