4-Methoxy-3,6,6-trimethyl-2-cyclohexenone (2e).—A solution of methylmagnesium iodide, from 360 mg of magnesium and 1 ml of methyl iodide in 50 ml of ether, was added dropwise over a 0.5-hr period to an ice-cold solution of 1.55 g of keto ether **3c** in 25 ml of dry ether and the mixture was stirred at room temperature for 14 hr. Saturated ammonium chloride solution (100 ml) was added and the ether solution was separated and evaporated. A suspension of 1.27 g of chromium trioxide in 20 ml of acetic acid was added to a solution of the residual carbinol stereoisomer mixture **4b** (1.62 g) in 10 ml of acetic acid and the mixture was kept at room temperature for 4 hr. It then was poured into water and extracted with ether. Evaporation of the extract, chromatography of the residue (0.97 g) on alumina (activity IV), and elution with hexane yielded an oil whose distillation gave 780 mg of ketone **2e**: bp 75° (0.5 Torr); uv (EtOH) λ_{max} 232 nm (ϵ 9900); ir (neat) 5.98 (s, C=O), 6.12 μ (m, C=C); pmr δ 1.12 (s, 3, Me), 1.16 (s, 3, Me), 1.0–2.3 (m, 2, CH_2), 1.99 (t, 3, J = 2 Hz, olefinic Me), 3.43 (s, 3, OMe), 3.98 (m, 1, OCH), 5.74 (m, 1, olefinic H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.51; H, 9.69.

Dienones 7.—A mixture of 500 mg of ketone **3a** and 1.3 g of selenium dioxide in 4 ml of water and 20 ml of dioxane was refluxed for 30 hr. It was filtered and the filtrate was diluted with water and extracted with ether. The extract was evaporated and the residue (390 mg) was chromatographed on alumina (activity IV). Elution with 20:1 pentane–ether gave 70 mg of liquid 4,4-dimethyl-2,5-cyclohexadienone (**7a**), ir and pmr identical with those cited in the literature.[4,7]

A solution of 9.6 g of keto ester **3d**[2d] in 125 ml of 0.5 N aqueous potassium hydroxide and 125 ml of methanol was kept at room temperature under nitrogen for 10 min. It was brought to pH 6 with acetic acid and evaporated under vacuum at room temperature. Extraction of the residue with ether, evaporation of the extract, and distillation of the residue gave 5.0 g of liquid 4,4-dimethyl-6-hydroxy-2-cyclohexenone (**3e**): bp 50° (0.2 Torr); ir (neat) 2.86 (m, OH), 5.92 (s, C=O), 6.15 μ (m, C=C); pmr δ 1.19 (s, 3, Me), 1.27 (s, 3, Me), 1.89 (d, 1, J = 13 Hz, H-5), 2.12 (dd, 1, J = 7, 2 Hz, H-5), 4.38 (dd, 1, J = 13, 7 Hz, H-6), 5.92 (d, 1, J = 10 Hz, H-2), 6.68 (dd, 1, J = 10, 2 Hz, H-3). A mixture of 2.8 g of the latter and 9.3 g of bismuth trioxide in 40 ml of acetic acid was kept at 100° for 10 min. It then was cooled, diluted with ether, and filtered. The precipitate was washed thoroughly with ether and the combined washings and filtrate were washed with saturated sodium bicarbonate solution and with water and evaporated. Distillation of the residue yielded 1.5 g of liquid 4,4-dimethyl-2-hydroxy-2,5-cyclohexadienone (**7b**): bp 53–54° (0.3 Torr); uv (EtOH) λ_{max} 238 nm (ϵ 6300), 283 (2440); ir (neat) 2.92 (m, OH), 6.06 (br s, C=O), 6.23 μ (w, C=C); pmr δ 1.31 (s, 6, Me_2), 5.98 (d, 1, J = 2 Hz, H-3), 6.18 (d, 1, J = 10 Hz, H-6), 6.82 (dd, 1, J = 10, 2 Hz, H-5).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.31; H, 7.50.

A mixture of 1.4 g of **7b**, 2.2 g of anhydrous potassium carbonate, and 5 ml of methyl iodide in 70 ml of dry acetone was stirred at room temperature for 18 hr. It was filtered and the filtrate was evaporated. Chromatography of the residue (1.6 g) on alumina (activity II) and elution with 10:1 hexane–ether yielded 720 mg of oil whose distillation produced liquid 4,4-dimethyl-2-methoxy-2,5-cyclohexadienone (**7c**): bp 81° (0.3 Torr); uv (EtOH) λ_{max} 238 nm (ϵ 9200), 283 (3100); ir (neat) 6.05 (s, C=O), 6.15 (s, C=C), 6.26 μ (s); pmr δ 1.31 (s, 6, Me_2), 3.62 (s, 3, OMe), 5.71 (d, 1, J = 2 Hz, H-3), 6.18 (d, 1, J = 10 Hz, H-6), 6.79 (dd, 1, J = 10, 2 Hz, H-5).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found C: 70.75; H, 7.96.

A mixture of 26.8 g of keto ether **9**[6] and 23.2 g of selenium dioxide in 192 ml of glacial acetic acid and 1.5 l. of dry *tert*-amyl alcohol was refluxed under nitrogen for 24 hr. It was filtered and the filtrate was concentrated at atmospheric pressure and finally evaporated fully under vacuum. A methylene chloride solution of the residual oil was washed with 5% sodium hydroxide solution and saturated brine solution, dried over potassium carbonate, and evaporated. Distillation of the residue gave 20.4 g of dienone **7c**, physical properties identical with those of the above sample.

4-Methoxy-3,6,6-trimethyl-2,4-cyclohexadienone (1a).—A solution of 180 ml of ethereal 1.5 M methyllithium was added to a stirring solution of 20.4 g of **7c** in 300 ml of ether under nitrogen at such rate as to assure gentle refluxing. After 14 hr water was added and the organic solution was separated, dried over potassium carbonate, and evaporated. The residual ketol **8** (22.3 g) [ir (neat) 2.90 (m, OH), 5.95 (m, C=C), 6.11 μ (m); pmr δ 1.05 (s, 3, Me), 1.11 (s, 3, Me), 1.37 (s, 3, carbinol Me), 3.57 (s, 3, OMe), 4.54 (s, 1, β-methoxy olefinic H), 5.53 (broad s, 2, olefinic Hs)] was used in the next reaction without further purification. Dry chromium oxide (13.5 g) was added to a stirring solution of 21.3 g of pyridine, distilled from barium oxide, in 350 ml of methylene chloride. After 15 min 2.78 g of **8** in 5 ml of methylene chloride was added to the mixture and stirring was continued for 15 min. The mixture was poured into ether and washed with 5% sodium hydroxide solution and 10% cupric sulfate solution. The organic solution was dried over magnesium sulfate and evaporated. Distillation of the residue gave 1.77 g of liquid ketone **1a**: bp 55° (0.2 Torr); ir (neat) 6.01 (s, C=O), 6.10 (s, C=C), 6.32 μ (s); pmr δ 1.19 (s, 6, Me_2), 2.03 (s, 3, olefinic Me), 3.57 (s, 3, OMe), 5.04 (s, 1, H-5), 5.85 (s, 1, H-2).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.45; H, 8.42.

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Registry No.—**1a**, 42116-94-9; **1b**, 23438-76-8; **2a**, 23438-77-9; **2b**, 42116-96-1; **2c**, 42116-97-2; **2d**, 38770-37-5; **2e**, 42116-99-4; **3a**, 1073-13-8; **3b**, 40441-34-7; **3c**, 42117-25-9; **3d**, 42117-26-0; **3e**, 42117-27-1; **5**, 42117-27-2; **6**, 42087-03-6; **7b**, 42117-29-3; **7c**, 42117-30-6; **8**, 42117-31-7; **9**, 42117-32-8; methyl iodide, 74-88-4; bis(dimethylamino)methoxymethane, 1186-70-5.

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An Improved Method for the Synthesis of Aliphatic Sulfinic Acids

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Despite their importance as polymerization activators[1] and as proposed intermediates in photochemical smog systems,[2] no simple one-step method appears to be available for the synthesis of aliphatic sulfinic acids in high yields and purity. For example, in the most important preparation,[3] the reduction of sulfonyl chlorides with zinc, iron, aluminium, or magnesium, the yields are reduced and the work-up is complicated by further reduction to disulfides and mercaptans.

Another favored method,[3] the treatment of organometallic compounds (RMgX and RLi) with sulfur dioxide, though preferable in cases where the sulfonyl chloride is unstable, suffers similarly from complications arising from competing side reactions. During the course of a study of the photochemical reactions of excited sulfur dioxide with hydrocarbons[4] we found it necessary to devise a synthesis capable of yielding

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(2) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, New York, N. Y., 1961, p 298.

(3) For reviews see W. E. Truce and A. M. Murphy, *Chem. Rev.*, **48**, 69 (1951); M. Quaedvlieg in "Enzyklopädie der organischen Chemie," E. Müller, Ed., Fourth ed, Band 9, Georg Thieme Verlag, Stuttgart, 1955, p 343.

(4) R. D. Penzhorn, L. Stieglitz, W. G. Filby, and K. Günther, *Chemosphere*, **3**, 111 (1973).

aliphatic sulfinic acids in gram amounts. We have observed that the direct oxidation of aliphatic mercaptans with *m*-chloroperoxybenzoic acid (MCPBA) (2 equiv) in methylene dichloride yields sulfinic acids in a high state of purity and in good yield. The experimental procedure is extremely simple and was applicable, in our hands, to all paraffinic isomers in the homologous series from ethyl to butyl. Preliminary experiments have also demonstrated that the reaction proceeds cleanly in the case of the analogous system thiophenol → benzenesulfinic acid.

From the stoichiometry the reaction appears to proceed *via* the intermediate sulfinic acid RSOH, which must then undergo a preferential rapid oxidation to sulfinic acid.

$$RSH \xrightarrow{[O]} RSOH \xrightarrow{[O]} RSO_2H$$

This reasoning is supported by our failure to observe disulfides in the reaction products by combined mass spectral–glc analysis. The latter are reported to be disproportionation products of sulfinic acids.[5]

$$2RSOH \longrightarrow RSH + RSO_2H$$

$$RSOH + RSH \longrightarrow RSSR + H_2O$$

Additionally we observed no trace of sulfonic acid in the freshly isolated sulfinic acids. Presumably *m*-chloroperoxybenzoic acid is too mild to further oxidize the sulfinic acid.

Experimental Section

Mercaptan (0.05 mol) was dissolved in methylene dichloride (10 ml) and cooled to −30° in a deep freeze. Similarly, MCPBA (0.1 mol) was dissolved in methylene dichloride (200 ml) and cooled to −30°. At 0.5-hr intervals MCPBA slurry (10 ml) was pipetted slowly with vigorous stirring (exothermic) into the mercaptan solution and the flasks were returned to the deep freeze. This procedure is necessary in order to prevent an excess of MCPBA building up in the presence of sulfinic acid. Neglect of the latter point leads to formation of sulfonic acid, which is difficult to separate in the purification stage. The reaction can be monitored for excess oxidant by removing a spot of reaction mixture and testing with acidified potassium iodide solution. After addition of all the oxidant solution the reaction flask was allowed to stand overnight at −30°, before filtration of the precipitated *m*-chlorobenzoic acid (MCBA). Removal of the last traces of the latter proved difficult. Our most successful method consisted of cooling the original solution to *ca.* −80° by immersing in liquid nitrogen and then rapidly filtering. Two repeats of this process gave an end product showing no MCBA peaks in its ir spectrum. After removal of the MCBA the procedure consisted solely of evaporating the solvent in a rapid nitrogen stream. The sulfinic acids remained as pale yellow oils or solids. A short period (30 min) in an evacuated desiccator (P_2O_5) removed the last traces of moisture. The yields ranged from 80 to 85%.

In a typical run *n*-butyl mercaptan (0.05 mol, 4.5 g) gave 4.95 g (81.5%) of *n*-butanesulfinic acid after purification: ir[6,7] ($CHCl_3$) 3000 (s), 2520 (s), 1470 (s), 1335 (s), 1130 (s, broad), 1075 (s, broad), 1015 (m, shoulder), 960 cm^{-1} (m, shoulder); mass spectrum[6] (70 eV) *m/e* (rel intensity, assignment) 137 (2.1, M + 1), 136 (4.3, M), 105 (16.4, C_4H_9SO), 80 (60, CH_4SO_2), 65 (24, SO_2H), 57 (100, C_4H_9).

Anal. Calcd for $C_4H_9SO_2H$: C, 39.39; H, 8.2; S, 26.22. Found: C, 39.1; H, 8.4; S, 26.08.

Evacuated samples maintained at low temperature (−30°) could be preserved for months without any noticeable decomposition (mass spectrum–glc). Samples warmed in either vacuum or air, however, rapidly undergo decay, turning to a deep orange yellow and precipitating white crystals.[8] For the purpose of long-term storage we have found it preferable to prepare the silver salts and store these under vacuum and low temperature. The latter can then be used at wish as a source of fresh sulfinic acid.

Registry No.—*m*-Chloroperoxybenzoic acid, 937-14-4; *n*-butyl mercaptan, 109-79-5; *n*-butanesulfinic acid, 5675-04-7.

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(8) W. G. Filby, unpublished observations.

Phosphorus Pentoxide–Methanesulfonic Acid. A Convenient Alternative to Polyphosphoric Acid

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Polyphosphoric acid (PPA) has been utilized extensively in organic synthesis. It is one of the most effective reagents for carrying out alkylation and acylation reactions on aromatic and olefinic systems. PPA is often the favored reagent for a variety of synthetic transformations such as dehydrations, the Fischer–Indole synthesis, the Beckmann rearrangement, the Schmidt rearrangement, and many others.[1-3] As has been widely recognized, however, polyphosphoric acid has certain unfortunate physical properties. It is extremely viscous and is virtually impossible to stir effectively or manipulate conveniently at temperatures below 60–90°. It is difficult to handle on a large scale, even at elevated temperatures. Some organics are only sparingly soluble in PPA, and, in any case, rates of dissolution are low. Hydrolysis of PPA in work-up procedures is always tedious.

To escape the difficulties encountered with polyphosphoric acid, we have developed a new reagent composed of a 1:10 solution by weight of phosphorus pentoxide in methanesulfonic acid.[4] This reagent, prepared by simply dissolving phosphorus pentoxide in methanesulfonic acid, is a mobile, colorless liquid that can be poured and stirred (even magnetically) without difficulty. Organic compounds dissolve readily in this medium. Unlike the related phosphorus pentoxide–trifluoromethanesulfonic acid reagent reported earlier from this laboratory,[5] the material is inexpensive, readily available, and safe to handle. Work-ups of phosphorus pentoxide–methanesulfonic acid reaction mixtures are easy and clean. The reagent can be destroyed conveniently with approximately three times

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(2) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, pp 894–905.

(3) F. Uhlig and H. R. Snyder, *Advan. Org. Chem.*, **1**, 35 (1960).

(4) The 1:10 ratio of components merely represents the limit of ready solubility of phosphorus pentoxide in methanesulfonic acid at room temperature. More concentrated reagents can easily be prepared at elevated temperatures. However, neither these nor more dilute solutions were investigated in any detail.

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