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.

(5) M. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

(6) F. Wudl, D. A. Lightmer, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 4099 (1967).

(7) S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

(8) W. G. Filby, unpublished observations.

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

PHILIP E. EATON,* GLENN R. CARLSON, AND JAMES T. LEE

Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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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

(1) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958).

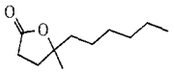
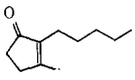
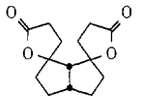
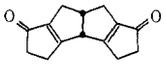
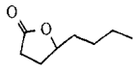
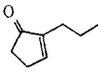
(2) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, pp 894–905.

(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.

(5) *Cf.* P. E. Eaton and R. H. Mueller, *J. Amer. Chem. Soc.*, **94**, 1014 (1972).

TABLE I
USE OF PHOSPHORUS PENTOXIDE–METHANESULFONIC ACID IN THE PREPARATION OF CYCLOPENTENONES AND AMIDES

Registry no.	Compound	Reaction conditions	Registry no.	Product	Typical isolated yield, %	Literature yield with PPA, %
7011-83-8		33 hr, 25°, 1:80[a]	1128-08-1		92	92[b]
36269-13-3		96 hr, 45°, 1:75 5 hr, 80°, 1:75 114 hr, 35°, 1:20 to 1:100[c]	36269-14-4		75–85[d]	65–70[e]
104-50-7		24 hr, 60°, 1:40	24105-07-5		33[f]	
			31863-60-2		24	52[g] (combined products)
501-52-0	Phenylpropionic acid	6 hr, 50°, 1:75	83-33-0	1-Indanone	87	93[h]
574-66-3	Benzophenone oxime	48 hr, 50°, 1:25 1 hr, 100°, 1:25	93-98-1	Benzanilide	95 90	99[i]
100-64-1	Cyclohexanone oxime	1 hr, 100°, 1:25	105-60-2	ε-Caprolactam	96	89[i]
629-31-2	Heptaldoxime	1 hr, 100°, 1:25	628-62-6	Heptamide	90[j]	92[k]

[a] Weight ratio, substrate:reagent. [b] Reference 7b. [c] The yield did not vary significantly over this range. At 1:10 the yield fell off substantially. In general, moderate temperature and a high ratio of reagent to reactant give the cleanest reactions. [d] Crystallized from isopropyl alcohol; mp 209–210°. [e] Reference 5. [f] Distilled at 58° (3 Torr) and separated by glpc (6 ft × 0.25 in., 10% Carbowax 20M on 60/80 Chromosorb W, 100°). [g] Reference 7e. [h] References 7f and 7g. [i] Reference 8a. [j] No trace of nitrile was detected in the crude reaction product. [k] Reference 8b.

its weight of water or with saturated aqueous sodium bicarbonate solution.[6]

Table I illustrates the utility of the phosphorus pentoxide–methanesulfonic acid reagent for two types of transformations classically performed in polyphosphoric acid, namely, the preparation of cyclopentenones *via* the intramolecular acylation of olefin acids or their lactones[7] and the preparation of amides *via* the Beckmann rearrangement.[8] In all cases, the isolated yield using 1:10 phosphorus pentoxide–methanesulfonic acid compares favorably with the best yield reported for the same transformation carried out in polyphosphoric acid. In fact, the reaction of each substrate in the new reagent seems to mimic that in polyphosphoric acid in terms of relative rate, product distribution, and yield. No doubt, phosphorus pentoxide–methanesulfonic acid could be substituted usefully in other reactions brought about by PPA.[9] Logically, the two reagents can be expected to have similar chemical limitations.[10]

The important reactant in the phosphorus pentoxide–methanesulfonic acid reagent is not certain; most probably it is a very active mixed anhydride. Although methanesulfonic anhydride is clearly present in the phosphorus pentoxide–methanesulfonic acid mixture, as observed by nmr, appropriate methanesulfonic anhydride–methanesulfonic acid solutions are less effective in carrying out these transformations; the reaction rates are slower, and product yields are generally poorer. Pure methanesulfonic acid will not promote the reactions considered here under comparable conditions.

(6) Quenching on ice is generally not recommended, as methanesulfonic anhydride, present in the mixture, precipitates and is only slowly hydrolyzed by cold water. The anhydride (mp 66–67°) is easily extracted into organic solvents and can be a bothersome contaminant. The hydrolysis of the anhydride is rapid at room temperature, requiring only 5–10 min. Quenching with aqueous sodium bicarbonate solution assures almost instantaneous hydrolysis of the anhydride, but this practice is less convenient, as extensive foaming occurs.

(7) (a) K. Biemann, G. Büchi, and B. H. Walker, *J. Amer. Chem. Soc.*, **79**, 5558 (1957); (b) C. Rai and S. Dev, *J. Indian Chem. Soc.*, **34**, 178 (1957); (c) T. M. Jacob and S. Dev, *ibid.*, **36**, 429 (1959); (d) T. M. Jacob, P. A. Vatakencherry, and S. Dev, *Tetrahedron*, **20**, 2815, 2821 (1964); (e) M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 2955 (1958); (f) R. C. Gilmore, Jr., *J. Amer. Chem. Soc.*, **73**, 5879 (1951); (g) G. Metz, *Synthesis*, 612 (1972).

(8) (a) E. C. Horning and V. L. Stromberg, *J. Amer. Chem. Soc.*, **74**, 2680 (1952); (b) *ibid.*, **74**, 5151 (1952).

(9) Following our recommendation, R. L. Cargill and T. E. Jackson, *J. Org. Chem.*, **38**, 2125 (1973) (footnote 17), have utilized methanesulfonic acid containing phosphorus pentoxide to effect the intermolecular acylation of cyclohexene with acrylic acid.

(10) J. K. Groves, *Chem. Soc. Rev.*, **1**, 73 (1972).

Experimental Section

Methanesulfonic acid (technical grade, Eastman Organic Chemicals) must be distilled before use for clean work-ups and good yields. Distillation under vacuum is recommended to avoid thermal decomposition that begins at temperatures of about 140–150°. The material used distilled at 108° (0.25 Torr) as a clear, colorless liquid containing less than 1 mol % methanesulfonic anhydride as determined by nmr. γ-Octanoic lactone and phenylpropionic acid were obtained from Aldrich Chemical Co.; the former was used directly, but the latter was recrystallized from heptane prior to use. All oximes were prepared according to literature procedures and were recrystallized to constant melting point.

Preparation of 1:10 Phosphorus Pentoxide–Methanesulfonic Acid Solution.—In a typical experiment, freshly distilled methanesulfonic acid (360 g) was placed in a 500-ml, three-necked flask fitted with an efficient mechanical stirrer (important) and a calcium chloride drying tube. Phosphorus pentoxide (36 g, weighed out in a drybox) was added in one portion and generally dissolved in 1–2 hr. The reagent could be used immediately or could be stored in a stoppered flask for later use. Slight yellowing occurred on long storage, but this did not effect the efficacy of the reagent to any noticeable degree.

Preparation of Dihydrojasmone.—The following procedure is typical for the preparation of cyclopentenones from lactones using the 1:10 phosphorus pentoxide–methanesulfonic acid reagent. A 4.91-g portion of γ-methyl-γ-decanolactone[11] was added in small portions to 410 g of rapidly stirred 1:10 phosphorus pentoxide–methanesulfonic acid. The homogeneous reaction

(11) P. E. Eaton, G. F. Cooper, R. C. Johnson, and R. H. Mueller, *J. Org. Chem.*, **37**, 1947 (1972).

mixture was stirred at 25° for 33 hr. The yellow solution was transferred to a 500-ml separatory funnel and added dropwise to 1 l. of water. The aqueous mixture was stirred rapidly for 5–10 min to ensure hydrolysis of methanesulfonic anhydride and was then extracted with chloroform (4 × 300 ml). The extract was washed once with dilute aqueous sodium bicarbonate (200 ml) and once with water, dried over magnesium sulfate, and concentrated. The fragrant oil remaining was distilled at 90–91° (2 Torr) to give 4.08 g (92%) of dihydrojasmone in 97% purity as judged by glpc (10 ft × 0.125 in., 15% OV-101 on 60/80 Chromosorb G, 200°). The semicarbazone was prepared, mp 176–177° (lit.[12] mp 175–176°).

Preparation of ε-Caprolactam.—The following is a typical preparation of amides from oximes using 1:10 phosphorus pentoxide–methanesulfonic acid. A 2.0-g portion of cyclohexanone oxime was added in small portions to 50 g of rapidly stirred 1:10 phosphorus pentoxide–methanesulfonic acid. Each batch of oxime was added only after the previous one had dissolved; the whole process required about 5 min. The colorless reaction mixture was then heated with stirring to 100°. One hour later the yellow solution was quenched in aqueous saturated sodium bicarbonate (200 ml) and extracted with chloroform (3 × 100 ml). The extract was dried with magnesium sulfate and evaporated. The crude product was crystallized from ether–hexane to give 1.92 g (96%) of ε-caprolactam as colorless crystals, mp 68–69° (lit.[8a] mp 65–68°).

Acknowledgment.—This work was supported generously by the National Science Foundation and the National Cancer Institute of the National Institutes of Health. G. R. C. is grateful to the National Institute of Allergy and Infectious Diseases of the NIH for a postdoctoral fellowship.

Registry No.—Phosphorus pentoxide–methanesulfonic acid, 39394-84-8.

(12) H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, **7**, 245 (1924).

An Improved Aromatization of α-Tetralone Oximes to *N*-(1-Naphthyl)acetamides[1]

MELVIN S. NEWMAN* AND WILLIAM M. HUNG

Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210

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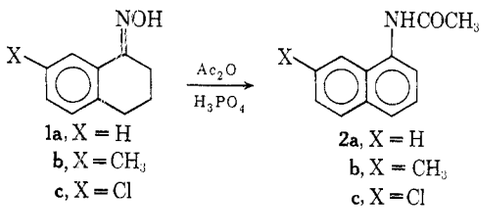
The conversion of oximes of substituted cyclohexenones to aromatic amines has been carried out frequently by heating in acetic acid–acetic anhydride containing dissolved hydrogen chloride or hydrogen bromide. This reaction, originally discovered by Semmler,[2] has been applied to methylated cyclohexenones,[3] tetralones,[4,5] and 1- and 4-keto-1,2,3,4-tetrahydrophenanthrenes,[5] although the yields rarely exceeded 50%. Because of the potential value of this type of intramolecular oxidation–reduction reaction for the synthesis of intermediates needed for the synthesis of polycyclic aromatic compounds, we decided to seek an improved method for carrying out such reactions.

We have found that on heating the oxime in acetic anhydride and anhydrous phosphoric acid at 80° for 30 min the yield of amine lies in the 82–93% region. By this method we have converted the oximes of α-tetralone (**1a**), 7-methyl-α-tetralone (**1b**), 7-chloro-α-tetralone (**1c**), and 4-keto-1,2,3,4-tetrahydrophenanthrene (**3**) into the corresponding acetylamino compounds (and/or amines) in 82, 91, 93, and 82% yields, respectively.



1a, X = H
b, X = CH_3
c, X = Cl

2a, X = H
b, X = CH_3
c, X = Cl

In one attempt to treat the oxime of 6-methoxy-α-tetralone under the new conditions, such a mixture of products was obtained (including nuclear acetylated material) that no further study of this compound was made.

Experimental Section

α-Tetralone (**1a**) and 6-methoxy-α-tetralone were purchased from the Aldrich Chemical Co., Milwaukee, Wis. 7-Methyl-α-tetralone (**1b**) was prepared as described.[6] 7-Chloro-α-tetralone[4a] (**1c**) was best prepared by heating a solution of 45 g of γ-(*p*-chlorophenyl)butyric acid[7] in 360 g of 115% polyphosphoric acid[8] at 90° for 30 min. The neutral fraction of the reaction products was crystallized from ether–petroleum ether (bp 35–60°) to yield 36.9 g (90%) of **1c**, mp 94.5–96.0°, pure enough for conversion to the oxime. Attempts to cyclize γ-(*p*-chlorophenyl)butyric acid with anhydrous hydrogen fluoride afforded **1c** in very low yield.

The oximes were prepared by refluxing a solution of the tetralone (0.1 mol), hydroxylamine hydrochloride (0.12 mol), pyridine (10 ml), and absolute ethanol (100 ml) for 4 hr. The oximes, after recrystallization from ether–petroleum ether, were obtained in 95–98% yield. The oxime **1c** was light sensitive.

Aromatization of Oximes.—In a typical experiment, 17.5 g (0.1 mol) of 7-methyl-α-tetralone oxime,[9] mp 100–101°, was added to a well-mixed solution of acetic anhydride (204 g, 2.0 mol) and anhydrous phosphoric acid (196 g, 2.0 mol).[10] The mixture was held at 80° for 30 min and the resulting light brown solution was poured in 1.5 l. of ice water. The solid was collected and washed with water to yield 12.8 g of *N*-(7-methyl-1-naphthyl)acetamide[6] (**2b**), mp 176–178°, after drying. The aqueous filtrate was made basic with sodium hydroxide and treated with 50 ml of acetic anhydride. The amide thus formed (5.2 g) was added to the first portion. The combined yield was 91%.

In a similar way **1a**,[11] mp 100.5–101.5°, **1c**,[4a] mp 124–125°, and **3**,[12] mp 174–175°, were converted into *N*-(1-naphthyl)acetamide (**2a**), mp 153–155°, *N*-(7-chloro-1-naphthyl)acetamide (**2c**), mp 196–197°, and *N*-(4-phenanthryl)acetamide,[12] mp 192–194°, in 82, 93, and 82% yields, respectively. In all cases, both amide and amine hydrochloride were formed. The yields reported include the amide formed from the amine as described.

Anal. Calcd for $C_{12}H_{10}ClNO$ (**2c**): C, 65.6; H, 4.6; N, 6.4; Cl, 16.2. Found: C, 65.8; H, 4.7; N, 6.4; Cl, 16.0.

In the case of **1c**, the reaction on 0.1 mol was carried out as described but with only one quarter of the amounts of acetic

(1) This research was supported by Grant No. CA-07394 from the National Institutes of Health.

(2) W. Semmler, *Ber.*, **25**, 3352 (1892). See also L. Wolff, *Justus Liebigs Ann. Chem.*, **322**, 351 (1902).

(3) F. M. Beringer and I. Ugelow, *J. Amer. Chem. Soc.*, **75**, 2635 (1953).

(4) (a) O. Schrader, *et al.*, *Ber.*, **63**, 1308 (1930); (b) A. Hardy, E. R. Ward, and L. A. Day, *J. Chem. Soc.*, 1979 (1956); (c) W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 386 (1967).

(5) W. Langenbeck and K. Weissenborn, *Ber.*, **72**, 724 (1939). See also F. M. Beringer, L. L. Chang, A. N. Fenster, and R. R. Rossi, *Tetrahedron*, **25**, 4339 (1969).

(6) L. Ruzicka and E. Morgeli, *Helv. Chim. Acta*, **19**, 377 (1936).

(7) S. Skraup and E. Schwamberger, *Justus Liebigs Ann. Chem.*, **462**, 135 (1928).

(8) We thank the FMC Corp., New York, N. Y., for a generous gift of 115% polyphosphoric acid.

(9) R. Huisgen and V. Vossius, *Monatsh. Chem.*, **88**, 517 (1957).

(10) Anhydrous phosphoric acid was prepared as described by R. E. Ferrel, H. S. Olcott, and H. Fraenkel-Conrat, *J. Amer. Chem. Soc.*, **70**, 2101 (1948).

(11) F. S. Kipping and A. Hill, *J. Chem. Soc.*, **75**, 150 (1899).

(12) J. W. Krueger and E. Mosettig, *J. Org. Chem.*, **3**, 340 (1938).