By means of this procedure III and IV were each converted to XI.

1,4-Dimethyl-2',3-dibromomethyl-2-phenylnaphthalene, XII. To a solution of 0.594 g. (0.002 mole) of dialcohol, XII, m.p. 156–157.5°, in 40 ml. of acetic acid there was added 12.5 ml. of 48% hydrobromic acid. After heating at reflux for 15 min., 6.25 ml. of 48% hydrobromic acid was added and heating continued one more hour. On cooling 0.620 g. (72%) of solid m.p. 148–150° (m) was filtered. After repeated crystallization from acetone-methanol, the melting point was 147–149°.

Anal. Calcd. for $C_{20}H_{18}Br_2$ (418.18): C, 57.44; H, 4.34. Found: C, 58.09, H, 4.59.

5,6-Dihydro-7,12-dimethylbenz(a)anthracene, X. A. *From the dibromo compound* XII. A solution of phenyllithium was prepared in an atmosphere of helium by adding slowly with stirring 1 ml. of bromobenzene to 0.157 g. (0.0227 g.-atom) of lithium suspended in 5 ml. of ether. The freshly prepared phenyllithium solution, followed by an ether wash, was transferred slowly in an atmosphere of helium to a stirred solution of 0.209 g. (0.0005 mole) of the dibromo compound, XII, in 20 ml. of benzene. The mixture was heated at reflux for 30 min., cooled, and decomposed with water and hydrochloric acid. The organic layer was washed with water, dried with sodium sulfate, and the solvent evaporated. The residual phenyl bromide was removed *in vacuo.* The residue was dissolved in cyclohexane and passed through Florisil. Cyclohexane was evaporated from the eluate and the residue crystallized from acetone-methanol to give 0.0671 g. (52%) of colorless[37] solid, m.p. 112–113°. This solid was identical with XII obtained below on the basis of mixed melting point and ultraviolet spectra determinations.

B. *From 7,12-Dimethylbenz(a)anthracene,* I. To a solution of 0.128 g. (0.0005 mole) of 7,12-dimethylbenz[a]anthracene. I, m.p. 122.5–123.1° in 50 ml. of 95% ethanol a small amount of catalyst (5% palladium on strontium carbonate) was added.[38] After several hours the catalyst was filtered and the solution was added to a hydrogenation flask containing 0.064 g. of prereduced catalyst (5% palladium on strontium carbonate); hydrogenation was slow and was continued overnight when 120% of the theoretical amount of hydrogen was absorbed. The catalyst was filtered and the solvent evaporated. The residue after crystallization from acetone-methanol gave 0.076 g. (59%) of colorless solid, m.p. 109–110.5° (m). After repeated crystallization from acetone-methanol and sublimation at 160° at 0.05 mm. the melting point was 112–113° (m.).

Anal. Calcd. for $C_{20}H_8$ (258.35); C, 92.98; H, 7.02. Found; C, 92.67; H, 7.04.

λ_{max} ($\log_{10} \epsilon$); 220 (4.486); 260 (4.918); 268 (4.981); 305 (3.955) λ_{min} ($\log_{10} \epsilon$) 234 (4.217); 264.5 (4.893); 284 (3.894).

In another experiment[39] the hydrogenation of 1.0 g. (0.0039 mole) of I using 50% palladium on strontium carbonate as the catalyst gave 0.731 g. (73%) of X, m.p. 112.3–112.8°. In this experiment the product was obtained subsequent to chromatography (see below) and crystallization from 95% ethanol.

Chromatographic separation of I *and* X. The separation of 1 mg. of I from 1 mg. X was accomplished on 1 g. of a 2:1 mixture of magnesia (Westvaco, Seasorb) and celite (Johns Manville) in an 8 mm. O.D. glass tube, under suction.

Fraction	Eluant		Eluate
1	10 ml. Cyclohexane		Nothing
2	2 ml. Cyclohexane		Nothing
3	10 ml. 1% Chloroform	99% Cyclohexane	X
4	10 ml. 1% Chloroform	99% Cyclohexane	Nothing
5	2 ml. 1% Chloroform	99% Cyclohexane	Nothing
6	10 ml. 20% Chloroform	80% Cyclohexane	I
7	10 ml. 20% Chloroform	80% Cyclohexane	I
8	2 ml. 20% Chloroform	80% Cyclohexane	Nothing

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(37) Repetition of this experiment likely would have given a higher yield.

(38) Prepared by the procedure of D. K. Banerjee, reference (35), footnote 33.

(39) Carried out by E. E. Smith.

[CONTRIBUTION FROM THE RESEARCH DIVISION, ELECTROCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

The Oxidation of Organic Substances by Potassium Peroxymonosulfate

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The reactions of a stable mixture of potassium peroxymonosulfate, potassium hydrogen sulfate, and potassium sulfate with a wide variety of organic substances have been investigated. The reactions with hydrocarbons, hydroxy compounds, carbonyl compounds, amines, nitrogen heterocycles, and with sulfur, phosphorus, and halogen compounds are described and discussed. The utility of peroxymonosulfates in halogenation reactions is also discussed. The behavior of peroxymonosulfates is compared with that of other inorganic peroxygen compounds and organic peroxyacids.

The existence of a peroxygen acid of sulfur was recognized nearly a century ago[1] but it was not until 1898 that Caro[2] demonstrated the existence of two such acids. It was known to Caro that salts of persulfuric acid (peroxydisulfuric acid, $H_2S_2O_8$) converted aniline to an insoluble dye (aniline black). When Caro treated aniline with a solution of ammonium persulfate in concentrated sulfuric acid, he obtained nitrosobenzene, but no aniline black. Three years later, Baeyer and Villiger[3] published conclusive evidence that Caro's acid was peroxymonosulfuric acid (H_2SO_5). It was not until 1910, however, that d'Ans and Friedrich[4] prepared pure, anhydrous peroxymonosulfuric acid.

The oxidation of aniline to nitrosobenzene by peroxymonosulfuric acid has already been cited;

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(1) T. S. Price, *Per-Acids and Their Salts,* Longmans, Green and Co., London, 1912, p. 10.

(2) H. Caro, *Z. angew. Chem.,* 845 (1898).

(3) A. Baeyer and V. Villiger, *Ber.* **34,** 853 (1901).

(4) J. d'Ans and W. Friedrich, *Ber.* **43,** 1880 (1910).

this is by no means the only example of the oxidation of an organic substance by peroxymonosulfuric acid or its salts. Peroxymonosulfuric acid and Baeyer's persulfuric reagent ($K_2S_2O_8$, H_2SO_4, and K_2SO_4) have been used in the preparation of lactones from cyclic ketones,[5] esters from ketones[6,7] glycols from olefins,[8] amine oxides from tertiary amines,[9] iodoxybenzene from iodobenzene,[10,11] and nitrosocyclohexane or cyclohexanone oxime from cyclohexylamine.[12]

The preparation of stable salts of peroxymonosulfuric acid has been described in a recent patent.[13] The reactions of a stable mixture of potassium peroxymonosulfate, potassium hydrogen sulfate, and potassium sulfate with a wide variety of organic substances have been investigated. The mixtures used in this investigation contained approximately 5% active oxygen[14] and consisted of approximately two moles of potassium peroxymonosulfate and one mole each of potassium bisulfate and potassium sulfate. Like peroxymonosulfuric acid, the salt mixture is a powerful oxidant with a wide range of application; unlike peroxymonosulfuric acid the mixture can be stored without appreciable loss of active oxygen and handled with negligible hazard to the user.

The mixed salts are moderately soluble in water; solutions approximately 1*M* with respect to potassium peroxymonosulfate can be prepared without difficulty at room temperature. The salt mixture used in our experiments formed strongly acidic solutions (about *p*H 2) because of the presence of the bisulfate ion. The peroxymonosulfate ion is stable in such acidic solutions. As Ball and Edwards[15] have shown, the active oxygen is gradually lost through decomposition reactions in alkaline solution.

Although potassium peroxymonosulfate is not appreciably soluble in common organic solvents, water-ethanol, water–acetic acid and water–ethanol–acetic acid mixtures have been employed successfully as solvents for the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture. A slurry of the mixed salts in glacial acetic acid has also proved to be an effective oxidant.

In addition to solubility, two other factors should be considered in predicting the behavior of peroxymonosulfate toward organic systems. The first of these factors is the oxidation potential of the peroxymonosulfate-bisulfate couple ($E^\circ = 1.44$v). If the standard potential for the organic couple is known, it is possible to predict whether or not the oxidation reaction is thermodynamically feasible. The second factor to be considered is the nature of the free radicals, ionic species, or indefinite intermediate complexes which might be obtained from peroxymonosulfate under various reaction conditions. In free radical reactions, for example, the peroxymonosulfate ion can theoretically liberate a hydroxyl radical and a sulfate ion-radical (Equation 1). One or the other of these radicals can be obtained from an organic peroxyacid, hydrogen peroxide, or peroxydisulfate ion (Equations 2, 3, 4). Thus peroxymonosulfate ion might be

$$HOOSO_3^- \longrightarrow HO\cdot + \cdot OSO_3^- \qquad (1)$$

$$RCOOOH \longrightarrow RCOO\cdot + \cdot OH \qquad (2)$$

$$HOOH \longrightarrow 2HO\cdot \qquad (3)$$

$$(O_3SOOSO_3)^{-2} \longrightarrow 2\cdot OSO_3^- \qquad (4)$$

expected to behave somewhat like all of these substances. Differences in behavior might also be expected, as peroxymonosulfate ion is the only one of the four substances capable of generating both an ion-radical and an uncharged radical. These expectations are at least partially confirmed by the fact that the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture effects both the Elbs persulfate oxidation of phenol (peroxydisulfate reaction) and the conversion of a cyclic ketone to a lactone (organic peroxyacid reaction).

An aqueous solution of the salt mixture converts toluene to benzoic acid and diphenylmethane to benzophenone. In both instances, prolonged stirring and heating of the reaction mixture is necessary due to the immiscibility of the aqueous and organic layers. Olefins can be converted to glycols or glycol esters depending upon the solvent system employed. Cyclohexene is converted to *trans*- rather than *cis*-cyclohexanediol. The preferential formation of this isomer may be an indication of *trans* addition by an electrophilic fragment of peroxymonosulfate, but it may also indicate that epoxides are intermediates in this reaction. Attempts to isolate the epoxides, however, have been unsuccessful. A terminal, as well as an internal double bond, can be hydroxylated by the salt mixture if sufficiently vigorous reaction conditions are employed.

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(5) A. Baeyer and Villiger, *Ber.* **32,** 3625 (1899).

(6) R. E. Marker, *J. Am. Chem. Soc.*, **62,** 2543 (1940).

(7) For a brief listing of the types of carbonyl compounds oxidized by Caro's acid or related peroxygen compounds, see W. vonE. Doering and L. Speers, *J. Am. Chem. Soc.*, **72,** 5515 (1950).

(8) Y. Ishii, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **54,** 58 (1951).

(9) L. W. Jones and E. B. Hartshorn, *J. Am. Chem. Soc.*, **46,** 1840 (1924).

(10) E. Bamberger and A. Hill, *Ber.* **33,** 533 (1900).

(11) I. Masson, E. Race, and F. E. Pounder, *J. Chem. Soc.*, 1669 (1935).

(12) I. Okamura and R. Sakurai, *Chem. High Polymers (Japan)*, **8,** 296 (1951).

(13) S. E. Stephanou, U. S. Patent **2,802,722** Aug. 13, 1957.

(14) Active oxygen, as the term is used here, refers to the oxygen in excess of that required to form the bisulfate, *i.e.*,

$$KHSO_5 \longrightarrow KHSO_4 + [O], \text{ where } [O] = \text{active oxygen.}$$

In terms of the structure of the peroxymonosulfate ion, $(HOOSO_3)^-$, the active oxygen is located in the perhydroxyl, *i.e.*, —O—O—H, group.

(15) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.* **78,** 1125 (1956).

The $KHSO_5$-$KHSO_4$-K_2SO_4 mixture readily converts 2-propanol to acetone and ethanol to acetic acid (or to ethyl acetate if an excess of ethanol is used). Acetaldehyde and acrolein could not be obtained from the corresponding alcohols despite a report[16] that potassium peroxydisulfate converts allyl alcohol to acrolein.

It appears that the $KHSO_5$-$KHSO_4$-K_2SO_4 composition studied does not effect the cleavage of vicinal glycols; in this respect, it differs from potassium peroxydisulfate, which cleaves vicinal glycols in the presence of silver ions.[17] On the other hand, it does convert phenol to hydroquinone in low yield; in this respect it resembles potassium peroxydisulfate.[18]

Moderate yields of lactones are obtained from the reaction of the salt mixture with cyclic ketones. In this case, its behavior resembles that of organic peroxyacids rather than that of inorganic peroxygen compounds. The latter reagents, including a $K_2S_2O_8$-H_2SO_4 mixture,[19] have a pronounced tendency to convert cyclic ketones to ω-hydroxyacids[20] or polyesters derived from these acids.[19,21]

Simple aromatic aldehydes are easily oxidized to the corresponding acids by the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture, but *o*-hydroxy aromatic aldehydes undergo the Dakin reaction (replacement of a formyl group by a hydroxyl group) when treated similarly. Diaryl ketones can be converted to esters by treatment with the salt mixture.

As expected from the behavior of peroxymonosulfuric acid, the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture readily converts primary aryl amines to nitroso compounds rather than to aniline black. Primary *n*-alkyl amines are oxidized to the corresponding acids by the salt mixture; for example, 2-phenethylamine is converted to phenylacetic acid. The salt mixture converts cyclohexylamine, a typical cycloalkylamine, to the corresponding nitroso compound. Spectroscopic evidence indicates that *t*-butylamine is oxidized to a nitroso or nitro compound, but the identity of the product has not been conclusively proved. Secondary aliphatic amines are apparently unaffected by a solution of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture in dilute acetic acid. Pyridine is converted to pyridine-1-oxide by a slurry of the salt mixture in glacial acetic acid.

The $KHSO_5$-$KHSO_4$-K_2SO_4 mixture converts alkyl mercaptans to sulfonic acids and diaryl sulfides to sulfones in nearly quantitative yields. Triphenylphosphine is oxidized to triphenylphosphine oxide and iodobenzene is oxidized to iodoxybenzene by the salt mixture.

The free radical polymerization of typical vinyl monomers such as vinyl acetate, ethyl acrylate, and acrylonitrile is initiated by the salt mixture. However, ammonium peroxydisulfate has been found to be superior to $KHSO_5$-$KHSO_4$-K_2SO_4 mixture as an initiator for such polymerizations.

The $KHSO_5$-$KHSO_4$-K_2SO_4 mixture apparently does not bring about the coupling (dehydrodimerization) of compounds such as toluene, acetic acid, and nitriles. This observation is somewhat surprising in view of the fact that both hydrogen peroxide[22] and potassium peroxydisulfate[23] effect the coupling of the above substances.

Toluene can be converted to a benzyl halide by heating with a dry mixture of the $KHSO_5$-$KHSO_4$-K_2SO_4 composition and an alkali metal chloride or bromide. However, such mixtures appear to be indifferent toward most other organic substances, including simple olefins.

EXPERIMENTAL[24,25]

1. *Benzoic acid (from toluene).* Toluene (27.6 g.) was heated under reflux with an aqueous solution of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture (135 g. in 400 ml. of water) for 22 hr. The organic layer was removed and combined with the ether extracts of the aqueous layer. The ether solution was dried over anhydrous sodium sulfate and filtered. Distillation of the filtrate gave 20.0 g toluene and 5.0 g. of a solid acidic residue. After crystallization from hot water, the acidic solid was identified as benzoic acid, m.p. 121–122°., neut. equiv. 121, 122.

2. *Benzophenone.* The procedure was essentially the same as that employed in the oxidation of toluene, except that the reaction mixture was heated for 30 hr. The ketone was isolated as its 2,4-dinitrophenylhydrazone (m.p. 239–240°) by treating the recovered diphenylmethane with an ethanol solution of 2,4-dinitrophenylhydrazine containing a catalytic amount of hydrochloric acid.

3. *trans-Cyclohexanediol.* Cyclohexene (16.4 g.) was added slowly to a solution prepared by dissolving the $KHSO_5$-$KHSO_4$-K_2SO_4 composition (50.5 g.) in a mixture of glacial acetic acid (75 ml.), water (75 ml.), ethanol (75 ml.), and concd. sulfuric acid (50 ml.). The reaction was maintained at a temperature of 70–80° and stirred vigorously for 3 hr. The mixture was allowed to cool, diluted with water, and extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate and filtered. Distillation of the filtrate under reduced pressure (1 mm.) gave 10.2 g. of a liquid (b.p. 75–80°) which solidified on standing. After crystallization from an ethanol-petroleum ether (b.p. 65–110°) mixture, the solid *trans*-cyclohexanediol melted at 79°.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.1; H, 10.3. Found: C, 61.75, 61.67; H, 10.02, 9.93.

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[16] R. L. Datta and J. N. Sen, *J. Am. Chem. Soc.*, **39**, 747 (1917).

[17] F. P. Greenspan and H. M. Woodburn, *J. Am. Chem. Soc.*, **76**, 6345 (1954).

[18] W. Baker and N. C. Brown, *J. Chem. Soc.*, 2303 (1948).

[19] R. Robinson and L. H. Smith, *J. Chem. Soc.*, 371 (1937).

[20] M. Fling, F. N. Minard, and S. W. Fox, *J. Am. Chem. Soc.*, **69**, 2466 (1947).

[21] M. Hudlicky, *Chem. listy*, **45**, 3801 (1952).

[22] D. D. Coffman, E. L. Jenner, and R. D. Lipscomb, *J. Am. Chem. Soc.*, **80**, 2864 (1958).

[23] C. Moritz and R. Wolffenstein, *Ber.*, **32**, 2531 (1899).

[24] All melting points are uncorrected.

[25] The stable mixture of $KHSO_5$, $KHSO_4$ and K_2SO_4 used in all reactions was "Oxone" monopersulfate compound containing about 5% active oxygen (E. I. du Pont de Nemours & Co., Inc.).

TABLE I

OXIDATION OF ORGANIC COMPOUNDS WITH $KHSO_5$-$KHSO_4$-K_2SO_4 MIXTURES

Compound	Procedure	Product	Conversion, %[a,c]	Yield, %[b,c]
Toluene	1	Benzoic acid	14	50
Diphenylmethane	2	Benzophenone	2	10
Cyclohexene	3	*trans*-Cyclohexanediol	44	44
1-Dodecene	4	1,2-Dodecanediol	30[d]	37[d]
2-Propanol	5	Acetone	100	100
Ethanol	5	Ethyl acetate	100[e]	100[e]
Phenol	6	Hydroquinone	4	21
Cyclopentanone	7	Valerolactone	35	35
Cyclohexanone	7	Caprolactone	46	46
Benzaldehyde	8	Benzoic acid	70	70
Salicylaldehyde	9	Pyrocatechol	17	70
Benzophenone	10	Phenyl benzoate	69	77
p-Phenylenediamine	11	*p*-Dinitrosobenzene	100	100
2-Phenethylamine	12	Phenylacetic acid	24	24
Cyclohexylamine	13	Nitrosocyclohexane	32	32
Pyridine	14	Pyridine-1-oxide	13	13
Dodecyl mercaptan	15	Dodecylsulfonic acid	100	100
Diphenyl sulfide	16	Diphenyl sulfone	97	97
Triphenylphosphine	17	Triphenylphosphine oxide	100	100
Iodobenzene	18	Iodoxybenzene	72	72

[a] % Conversion = $\frac{\text{moles of product}}{\text{moles of limiting reactant}} \times 100$. [b] % Yield = $\frac{\text{moles of product}}{\text{moles of limiting reactant not recovered}} \times 100$. [c] The yields and conversions reported should not, in all cases, be regarded as the best obtainable. It is felt that many of the reported yields can be improved by modification of the techniques used in isolation of products and recovery of reactants. Some conversions might be improved if more favorable reaction conditions can be found. [d] The glycol was obtained by a two-step process. The yield and conversion reported are based on the glycol-olefin mole ratio. [e] Based on $KHSO_5$.

4. *1,2-Dodecanediol.* A mixture of the $KHSO_5$-$KHSO_4$-K_2SO_4 composition (61.4 g.), glacial acetic acid (75 ml.), ethanol (75 ml.), distilled water (75 ml.), concd. sulfuric acid (50 ml.), and 1-dodecene (33.6 g.) was stirred and heated under reflux for 3 hr. The mixture was allowed to cool and the organic (less dense) layer was removed and washed with four 25-ml. portions of 10% sodium chloride solution. The washed liquid was dried over anhydrous magnesium sulfate, filtered, and distilled, first at atmospheric pressure, then under reduced pressure. Two high-boiling fractions (I, b.p. 120–170°/7 mm., 11.5 g.; II, b.p. 170–235°/7 mm., 5.2 g.) were obtained. The infrared spectra of these fractions indicated that they probably consisted of the mono- and diacetates of 1,2-dodecanediol. A portion (5.8 g.) of Fraction I was boiled under reflux with alcoholic potassium hydroxide (5.0 g. potassium hydroxide, 30 ml. ethanol) for 5 hr. The reaction mixture was then concentrated to a volume of 15 ml. and poured into 350 ml. of hot water. After the mixture cooled, the product (a fragrant oil) was removed by extraction with ether (100 ml. in three portions). The ether solution was dried and filtered; evaporation of the ether left 3.2 g. of an oily residue which solidified on standing overnight. The crude product melted at 52–55° (reported[26] for 1,2-dodecanediol, m.p. 60–61°). Two crystallizations from methanol failed to raise the melting point or narrow the melting range. However, the infrared spectrum of the product left little doubt that it was 1,2-dodecanediol.

Anal. Calcd. for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95. Found: C, 71.81, 71.78; H, 12.59, 12.80.

5. *Acetone.* A 1-l. three necked flask was fitted with a total condensate, variable take-off distilling head, a mechanical stirrer and an addition funnel. The flask was charged with the $KHSO_5$-$KHSO_4$-K_2SO_4 (50.0 g.) and 2-propanol (200 ml.). The stirrer was started and concentrated sulfuric acid added at such a rate that the temperature of the reaction mixture was maintained at about 70°. A liquid, b.p. 57–65°, was distilled from the reaction flask. This liquid was redistilled through an 18-inch, silver mirrored Vigreux column. Aliquots of the distillate were withdrawn periodically and treated with Brady's 2,4-dinitrophenylhydrazine reagent. The resulting 2,4-dinitrophenylhydrazone melted at 127–128° and did not depress the melting point of authentic acetone 2,4-dinitrophenylhydrazone. The distilled acetone obtained weighed 10.2 g.

Ethanol was treated similarly. No acetaldehyde distilled from the reaction flask, but ethyl acetate was recovered from the reaction mixture.

6. *Hydroquinone.* Phenol (18.8 g.) was dissolved in 400 ml. of an aqueous (10%) sodium hydroxide solution. The resulting solution was chilled to 5–10° and stirred vigorously while 250 ml. of an aqueous solution of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture (61.4 g.) was added. The addition required 3.5 hr.; the reaction mixture was then allowed to come to room temperature (23°) and stand overnight. The reaction mixture was made strongly acidic and extracted with ether. The ether extracts were dried over anhydrous sodium sulfate and filtered. Distillation of the extracts yielded 14.8 g. of unchanged phenol. The acidic reaction mixture was boiled under reflux for 30 min., cooled, and again extracted with ether. The extracts were dried over anhydrous sodium sulfate and filtered. Removal of the ether by distillation gave 1.0 g. of a dark-colored, solid residue. After two crystallizations from dilute hydrochloric acid, the solid melted at 171–173° and did not depress the melting point of an authentic sample of hydroquinone.

7. *ε-Caprolactone.* An aqueous solution (400 ml.) of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture (150 g.) was added slowly to a cold (0–5°) mixture of cyclohexanone (49 g.) and water (250 ml.). The resulting mixture was stirred for 30 min., then neutralized with an aqueous solution of potassium carbonate. The aqueous layer was extracted with three 100-ml. portions of ether. The ether extracts were combined, dried over anhydrous sodium sulfate and filtered. Distillation of the extracts, first at atmospheric pressure, then under reduced pressure, gave 26 g. crude ε-caprolactone, b.p. 97–110°/14 mm., n_D^{22} 1.450.

The procedure used for the preparation of δ-valerolactone

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(26) D. Swern, G. N. Billen, and J. T. Scanlan, *J. Am. Chem. Soc.*, **68**, 1504 (1946).

was similar to the above, except that the solvent used was a mixture of water, ethanol and sulfuric acid.

8. *Benzoic acid* (*from benzaldehyde*). A solution of the $KHSO_5$-$KHSO_4$-K_2SO_4 (25.0 g.) in 150 ml. of distilled water was added cautiously to a solution of benzaldehyde (10.6 g.) n chloroform. Concentrated sulfuric acid was then added slowly to this mixture. The resulting slurry was swirled occasionally over a period of 2 days. The organic layer was removed and combined with the ether extracts of the aqueous layer. The combined extracts were dried over anhydrous sodium sulfate and filtered. The ether was evaporated from the filtrate and the solid residue crystallized from boiling water. The yield of benzoic acid (m.p. 122°, neut. equiv. 120, 119) obtained in this way was 8.4 g.

9. *Pyrocatechol.* One hundred fifty milliliters of a 20% aqueous solution of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture was added to a solution of 12.2 g. salicylaldehyde in 100 ml. of chloroform. Concentrated sulfuric acid (10 ml.) was added slowly to the vigorously stirred mixture. After addition of the acid, the reaction mixture was stirred for 8 hr., then poured into cold water. The organic layer was removed and combined with the chloroform extracts of the aqueous layer. The chloroform solution was dried over anhydrous sodium sulfate, filtered and distilled, first at atmospheric pressure, then under reduced pressure. Unchanged salicylaldehyde (18.2 g.) was obtained together with 2.1 g. pyrocatechol (m.p. 103°).

10. *Phenyl benzoate.* A thick paste prepared from 25 g. of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture and 25 ml. of concd. sulfuric acid was added in small portions to a solution of 7.0 g. of benzophenone in 25 ml. of glacial acetic acid. The mixture turned deep red and required intermittent cooling; the temperature was not allowed to exceed 35°. After 30 min., the reaction mixture was poured into a slurry of ice and water and the resulting solution extracted with ether. The extracts were dried in the usual manner. The residue which remained after removal of the ether was distilled under reduced pressure. The distillate was dissolved in warm ethanol, the resulting solution seeded with a crystal of benzophenone and allowed to stand for 48 hr. at 0°. The crystallized benzophenone (0.8 g.) was removed by filtration. The filtrate was heated to boiling, then distilled water was added until turbidity developed. After 24 hr., the crystallized phenyl benzoate (5.2 g., m.p. 67°) was collected. Two crystallizations from ethanol raised the melting point of the ester to 70.0–70.5°.

11. *p-Dinitrosobenzene.* A solution of 25.6 g. of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture in 200 ml. of water was added slowly, with swirling, to 5.4 g. of *p*-phenylenediamine in 100 ml. of water. The red precipitate of *p*-dinitrosobenzene was removed by filtration and air dried. The product weighed 6.8 g., and showed the characteristic behavior of *p*-dinitrosobenzene[27] when heated (turned brown at 184–186° and black at 243°).

12. *Phenylacetic acid.* A mixture of the $KHSO_5$-$KHSO_4$-K_2SO_4 composition (30 g.), 2-phenethylamine (12.1 g.), and distilled water (150 ml.) was heated under reflux for 24 hr. The mixture was allowed to cool, then extracted with ether. The ether solution was dried over anhydrous sodium sulfate, filtered, and distilled (first at atmospheric pressure, then under reduced pressure). After 3.2 g. of phenylacetic acid (b.p. 90–94°/1 mm.; neut. equiv. 132, 130) had been collected, considerable decomposition occurred leaving a dark, tarry pot residue which weighed 5.1 g. The original reaction mixture was made basic and again extracted with ether. Only a trace of an unidentified dark-colored liquid was isolated from the ether extracts.

13. *Nitrosocyclohexane.* A solution of 25 g. of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture in 150 ml. of water was added rapidly and with vigorous agitation to a solution of 10.0 g. of cyclohexylamine in 50 ml. ether. An exothermic reaction occurred. The mixture was allowed to cool to room temperature and made basic by the addition of solid sodium carbonate. The ether layer and a yellow solid which had precipitated were separated from the aqueous phase of the mixture. The aqueous solution was extracted continuously with ether for a period of 18 hr. The ether solutions were combined, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The crude nitrosocyclohexane (3.7 g., precipitate plus residues from ether solution) thus obtained was recrystallized from ethanol, giving a pale yellow product which melted at 114–115°.

14. *Pyridine-1-oxide.* A vigorously stirred mixture of pyridine (15.8 g.), glacial acetic acid (120 ml.), distilled water (17 ml.), and the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture (61.4 g.) was maintained at 70° for 3 hr. A second portion of the salt mixture (30.7 g.) was added and the stirring continued (at 70°) for 18 hr. The mixture was allowed to cool and the solids were removed by filtration. The liquid portion of the mixture was concentrated to a volume of about 40 ml. by evaporation of the acetic acid under reduced pressure. Distilled water (40 ml.) was added to the mixture, which was again concentrated, this time to a volume of about 10 ml. This final concentrate was made strongly basic by the addition of solid sodium carbonate and a few milliliters of distilled water. The basic mixture was shaken with 100 ml. of chloroform and allowed to stand overnight. The solids were removed by filtration and washed with two 25-ml. portions of chloroform. The combined chloroform solutions were distilled leaving as a residue 2.5 g. of crude pyridine-*1*-oxide. A picrate prepared from the oxide melted at 182.5–183.0° with sintering at 179°.

15. *Dodecylsulfonic acid.* Dodecyl mercaptan (5.0 g.) was shaken with 150 ml. of a 25% aqueous solution of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture for a period of 30 min. The mixture was then placed in a liquid-liquid extraction apparatus along with 250 ml. of concd. hydrochloric acid. The resulting solution was continuously extracted with ether for 12 hr. The ether layer was removed and dried over anhydrous sodium sulfate. Evaporation of the ether left a residue of 6.2 g. of dodecylsulfonic acid (m.p. 43–44°; neut. equiv. 250).

16. *Diphenyl sulfone.* Diphenyl sulfide (11.0 g.) was added over a 20-min. period to a solution prepared from the following: glacial acetic acid (100 ml.), absolute alcohol (100 ml.), distilled water (100 ml.), concd. sulfuric acid (50 ml.), and the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture (35 g.). The mixture was stirred for 5 hr., then diluted with distilled water. The organic layer was removed and combined with the chloroform extracts of the aqueous layer. The chloroform solution was dried over anhydrous sodium sulfate and filtered. Removal of the chloroform from the filtrate gave 12.5 g. of diphenyl sulfone (m.p. 120–121°). Crystallization from ethanol–petroleum ether (b.p. 65–110°) raised the melting point of the sulfone to 124°.

17. *Triphenylphosphine oxide.* One hundred milliliters of a 20% aqueous solution of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture was added to a solution of 5.0 g. of triphenylphosphine in 50 ml. of ethanol. The temperature of the mixture rose to 70°, and the rate of addition was adjusted so that this temperature was maintained until the addition was complete. The mixture was stirred briskly for 4 hr., then diluted with cold water and extracted with benzene. Crude triphenylphosphine oxide was obtained in quantitative yield by evaporating the benzene solution to dryness. Crystallization of the crude oxide from a benzene–petroleum ether (b.p. 65–110°) mixture gave a pure product which melted at 156–157°.

18. *Iodoxybenzene.* Iodobenzene (20.0 g.) was added slowly to a mixture prepared by dissolving 35 g. of the $KHSO_5$-$KHSO_4$-K_2SO_4 in a slurry of ice (150 g.) and concd. sulfuric acid (100 g.). The resulting mixture was stirred for 4 hr., then diluted with water. The white precipitate which formed was removed by filtration and recrystallized from boiling water. The yield of iodoxybenzene (m.p. 235°,

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explodes!, equivalent weight as oxidizer 67.0, 64.6) thus obtained was 16.0 g.

TABLE II

HALOGENATIONS WITH ALKALI METAL HALIDE $KHSO^5$-$KHSO_4$-K_2SO_4 MIXTURES

Compound	Halide	Procedure	Product	Conversion,[a] %	Yield,[a] %
Toluene	NaCl	19	Benzyl chloride	15[b]	15[b]
Toluene	NaBr	19	Benzyl bromide	21[b]	21[b]
2-Octene	KBr	20	2,3-Dibromo-octane (?)	59[c]	59[c]

[a] As defined in Table I. [b] Based on halide. [c] Based on octene.

19. *Benzyl chloride.* An intimate mixture of powdered sodium chloride (11.7 g.), the $KHSO_5$-$KHSO_4$-K_2SO_4 composition (50.5 g.), and toluene was heated under reflux for 15 hr. The solids were removed by filtration and the liquid was distilled through an 18-inch Vigreux column. Four grams of benzyl chloride (b.p. 73–77°/17 mm., m.p. −47° to −45°, n_D^{25} 1.5322) were obtained.

20. *2,3-Dibromooctane.* An aqueous potassium bromide solution (23.8 g. potassium bromide, 50 ml. distilled water) and 2-octene (11.2 g.) were added simultaneously to a stirred solution of 61.4 g. of the $KHSO_5$-$KHSO_4$-K_2SO_4 mixture in 250 ml. of distilled water. The addition required about 30 min.; stirring was continued for 2 hr. after the addition was complete. The excess bromine was destroyed by the addition of solid sodium sulfite and the product extracted with methylene chloride (100 ml. in three portions). The extracts were dried over anhydrous magnesium sulfate, filtered, and distilled, first at atmospheric pressure, then under reduced pressure. The major fraction boiled at 105–12°/11 mm. and was identified as a saturated bromoalkane (presumably 2,3-dibromooctane), as it gave a precipitate when treated with alcoholic silver nitrate, but gave negative tests for active unsaturation.

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Synthesis of Pyrimidine-5-carboxaldehydes by the Reimer-Tiemann Reaction

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A study of the structural requirements for the synthesis of pyrimidine-5-carboxaldehydes by the Reimer-Tiemann reaction has shown that the reaction is successful with two methyl and one hydroxyl substituents in the pyrimidine nucleus. The hydroxyl group may be in either the 2- or 4-position. The reaction fails with 4-hydroxypyrimidine and its 6-methyl derivative indicating the necessity for the electron release characteristics of two methyl groups. Monohydroxydimethyl-, di-, and trihydroxypyrimidines give pyrimidine-5-carboxaldehydes. A variety of carbonyl derivatives of the pyrimidine aldehydes are described.

Pyrimidine aldehydes have not been investigated in detail. Their synthesis from acyclic intermediates[1] has not proved to be useful, but a variety of substituted pyrimidines has been converted to aldehydes by standard reactions. Thus, aldehydes have been obtained by ozonolysis of ethylenic groups,[2] by hydrolysis of nitrosomethyl groups,[3] and by suitable conversions of cyano,[4] carboxy,[5] trichlorohydroxyethyl,[6] and hydroxymethyl[7] groups. Formyl groups, or derivatives thereof, have been introduced directly by acylation reactions[8,9,10] and by the Reimer-Tiemann reaction.[6] The last appears to be the most generally useful reaction yet described. Aldehydes have been prepared from 2-amino or alkylamino-4-hydroxy; 2,4-dihydroxy; and 2-piperidinyl or phenyl-4,6-dihydroxy types.[6] Our study was undertaken to extend the Reimer-Tiemann reaction to additional types and to determine minimum structural requirements for activation of the nucleus by electron releasing groups in this reaction.

The pyrimidines converted to aldehydes in the present study are listed in Table I. The aldehydes were prepared, in 13–42% yields, by treating a water-ethanol solution of the pyrimidine with potassium hydroxide and chloroform at 80° for one hour. The potassium salt of the aldehyde

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