One crystallization from benzene and several from methanol elevated the melting point to 181.5–182°.

Anal. Calcd. for $C_{11}H_6Cl_4O_4$: Cl, 41.23. Found: 41.02, 41.18.

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Derivatives of *sym*-Trialkylbenzenes

2,4,6-Triethylbenzonitrile.—A mixture of 60 g. of 2,4,6-ethylbromobenzene,[1] 5.0 g. of cuprous cyanide and 60 ml. of pyridine was heated under reflux for eleven hours, allowed to cool somewhat and poured into 400 ml. of dilute ammonium hydroxide solution. The nitrile was extracted with a mixture of benzene and ether. The solution was washed with water and with dilute ammonium hydroxide solution, dried over calcium chloride and distilled. The nitrile boiled at 150–151° (24 mm.); n^{20}_{D} 1.5201; d^{25}_4 0.9366; yield 64%.

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.37; H, 9.15. Found: C, 83.23; H, 9.12.

Dillingham and Reid[2] made this compound by another method; they reported the boiling point as 108.5° (2 mm.) and the density as d^{25}_4 0.9356, but did not include an analysis.

3,5-Dinitro-2,4,6-triethylbenzonitrile.—Two grams of 2,4,6-triethylbenzonitrile was added slowly to 20 ml. of fuming nitric acid which had been cooled to 0°. The mixture was allowed to stand for thirty minutes in an ice-bath and was then poured into 200 ml. of water. The product was recrystallized from methanol; m. p. 69–70.5°; yield 1.5 g.

Anal. Calcd. for $C_{13}H_{15}O_4N_3$: C, 56.30; H, 5.41. Found: C, 56.21; H, 5.57.

1-Ethyl-2,4,6-triisopropylbenzene.—2,4,6-Triisopropylbenzyl chloride was coupled with methylmagnesium iodide according to the method described for 4-*t*-butyl-2,6-dimethylbenzyl chloride.[3] 1,2-Di-(2,4,6-triisopropylphenyl)-ethane[4] was obtained in 63% yield. The alkylation product, 2,4,6-triisopropylethylbenzene, boiled at 101–103° (5 mm.); n^{20}_{D} 1.4927.

Anal. Calcd. for $C_{17}H_{28}$: C, 87.85; H, 12.15. Found: C, 88.21; H, 12.04.

Ethyl 4-*t*-Butyl-2,6-dimethylbenzyl Ether.—This compound was produced in an attempt to reduce 4-*t*-butyl-2,6-dimethylbenzyl chloride. To a solution of 15 g. of sodium hydroxide pellets in 220 ml. of 95% ethanol was added 25 g. of the chloride. Three grams of aluminum powder was added slowly, with stirring, and the mixture heated under reflux for three hours. The ether, isolated in the usual way, boiled at 126–126.5° (7 mm.); n^{20}_{D} 1.5008; yield 78%.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.75; H, 10.98. Found: C, 82.02; H, 11.03.

Ethyl 2,4,6-Triisopropylbenzyl Ether.—This compound was produced in an attempt to reduce 2,4,6-triisopropylbenzyl chloride by a procedure similar to that used with 4-*t*-butyl-2,6-dimethylbenzyl chloride. The product, isolated in the usual manner, boiled at 132–134° (6 mm.); n^{20}_{D} 1.4928.

Anal. Calcd. for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.05; H, 11.50.

An attempt to brominate this ether converted it to bromomesitylene.

2,4,6-Triisopropylbenzyl Acetate.—A mixture of 10 g. of silver acetate, 15 g. of 2,4,6-triisopropylbenzyl chloride and 30 ml. of glacial acetic acid was heated for six hours on a steam-bath. The silver chloride was removed by filtration and the solvent evaporated under diminished pressure. The acetate boiled at 161–162° (13 mm.); n^{15}_{D} 1.5033; d^{20}_4 0.9536.

Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.19; H, 10.21. Found: C, 78.15; H, 10.44.

Hydrolysis of the acetate yielded 2,4,6-triisopropylbenzyl alcohol, m. p. 83–84°.[4]

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[1] Fuson and Corse, THIS JOURNAL, **60**, 2063 (1938).

[2] Dillingham and Reid, *ibid.*, **60**, 2606 (1938).

[3] Fuson, Denton and Kneisley, *ibid.*, **63**, 2652 (1941).

[4] Fuson, Horning, Ward, Rowland and Marsh, *ibid.*, **64**, 30 (1942).

Derivatives of 8-Chloroquinoline[1]

8-Chloroquinoline Picrate.—A 7.0-g. portion of picric acid (containing 10% water) was dissolved in 90 ml. of benzene. The solution was dried over anhydrous sodium sulfate, filtered, and added to a solution of 4.5 g. of 8-chloroquinoline[2] in 25 ml. of benzene. The yellow precipitate was collected, washed with benzene, and dried. The yield was 10.5 g. (97%); m. p. 178–180°. A sample was recrystallized from ethanol (70 ml./g.) for analysis, m. p. 178–180°.

Anal. Calcd. for $C_{15}H_9O_7N_4Cl$ (392.7): C, 45.88; H, 2.31. Found: C, 45.50; H, 2.11.

Thiourea Addition Compound of 8-Chloroquinoline.—This compound was obtained during an attempted preparation of 8-quinolinethiol from 8-chloroquinoline via the isothiuronium salt. A solution of 1.64 g. of 8-chloroquinoline in 15 ml. of absolute ethanol was boiled under reflux with 0.76 g. of thiourea for fifteen minutes; the thiourea gradually dissolved. On cooling, the clear solution deposited 1.0 g. (38%) of colorless needles, m. p. 131–132°. (The same result was obtained when the reaction mixture was boiled five hours.) The addition compound (0.8 g.) was recrystallized from ethanol for analysis; recovery 0.6 g., colorless needles, m. p. 132–133°. The compound gave positive sodium-fusion tests for nitrogen, halogen and sulfur, but was completely inert to hot alcoholic silver nitrate. This showed that it was not the desired 8-quinolineisothiuronium chloride, but an isomeric addition-compound of 8-chloroquinoline and thiourea.

Anal. Calcd. for $C_{10}H_{10}N_3SCl$ (239.7): C, 50.08; H 4.21. Found: C, 49.78; H, 4.34.

[1] This work was done under a contract recommended by the Committee on Medical Research between the Office of Scientific Research and Development and the University of Rochester.

[2] Claus and Scholler, *J. prakt. Chem.*, (2) **48**, 140 (1893).

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SOME HYDROXYPEROXIDES

The peroxides shown in Table I have been synthesized[1] in an anhydrous ethereal solution. Hydroxy dicarbethoxymethyl hydroperoxide and di-[hydroxy-dicarbethoxymethyl]-peroxide were prepared from ethyl oxomalonate,[2] while α,α'-dihydroxydiisoamyl peroxide and α,α'-dihydroxy-di-*n*-hexyl peroxide were prepared from isovaleric aldehyde and *n*-hexaldehyde, respectively. α,α'-Dihydroxy-di-*n*-hexyl peroxide was also prepared in good

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[1] Milas, Harris and Panagiotakos, THIS JOURNAL, **61**, 2430 (1939).

[2] Dox, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, 1941, p. 266.

TABLE I

SOME HYDROXY PEROXIDES

Peroxide	Formula	Active oxygen, % Calcd.	Active oxygen, % Found
Hydroxy dicarbethoxymethyl[a]	$C_7H_{12}O_7$	7.7	7.55
Di-[hydroxy dicarbethoxymethyl][b]	$C_{14}H_{22}O_{12}$	4.19	4.24 4.19
α,α'-Dihydroxydiisoamyl	$C_{10}H_{22}O_4$	7.76	7.60
α,α'-Dihydroxydi-*n*-hexyl[c]	$C_{12}H_{26}O_4$	6.84	6.69

[a] $d^{29}{}_{29}$ 1.226; n^{27}D 1.4392.
[b] $d^{29}{}_{29}$ 1.216; n^{27}D 1.4388.
[c] M. p. 62–63 °.

yields from aqueous 30% hydrogen peroxide and *n*-hexaldehyde.

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RECEIVED DECEMBER 31, 1945

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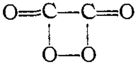
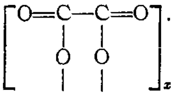
(3) From Part I of Ph.D. Thesis, M. I. T., 1939.

Diperoxalic Acid

When oxalyl chloride[1] was treated at 0° with an ice-sodium peroxide mixture, it was hoped to obtain a carbon peroxide, , or one of its polymers, 

$$\left[\begin{matrix} O= & C & - & C & =O \\ & | & & | & \\ & O & & O & \\ & | & & | & \end{matrix}\right]_x$$

. Neither one of these peroxides was obtained, but instead a small yield of diperoxalic acid. A higher yield of this diperacid was obtained by the following, somewhat different, procedure: To a solution of 19 g. of dry pyridine, 285 cc. of anhydrous ether containing 4 g. of hydrogen peroxide and maintained at −20°, was added, dropwise in the course of two hours and with vigorous stirring, a precooled (−10°) solution of 75 cc. of anhydrous ether containing 14.3 g. of oxalyl chloride. At the end of the reaction, the ether layer was decanted and the solid precipitate, which had separated out, extracted with two 100-cc. portions of anhydrous ether. The residue was then treated with an ice-cold mixture of 60 cc. of saturated sodium sulfate solution and 40 cc. of 85% orthophosphoric acid. The resulting mixture, after adding more solid sodium sulfate, was extracted with three 100-cc. portions of acetone which was combined with an equal volume of ether and the mixture dried and filtered. When the solvent was removed under reduced pressure, a highly viscous residue (2.2 g.) remained which failed to crystallize on standing for some time at 0°. This product was free from chlorine and nitrogenous products, and was found to be very soluble in water and chloroform. Diperoxalic acid is a powerful oxidizing agent, and, when treated with potassium iodide, it is reduced rapidly to oxalic acid.

Anal. Calcd. for $C_2H_2O_6$: (O), 26.3. Found: (O), 25.4, 25.7.

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RECEIVED DECEMBER 31, 1945

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(1) Prepared according to Staudinger, *Ber.*, **41**, 3563 (1908).

(2) From Part I of Ph.D. Thesis, M. I. T., 1939. Present address: Lowell Textile Institute, Lowell, Mass.

COMMUNICATIONS TO THE EDITOR

3-*n*-PENTADECYLCATECHOL

Sir:

Recently the synthesis of 3-*n*-pentadecylcatechol (Hydrourushiol) was described by H. S. Mason.[1] This compound, the dimethyl ether of which was first synthesized in low yield about thirty years ago by Majima and Tahara,[2] and later by Backer and Haack,[3] has attracted considerable interest in view of its close relationship to poison ivy "urushiol." The scheme of synthesis which Mason found gave the best results was essentially that employed by Backer and Haack for the preparation of the dimethyl ether. However, Mason markedly improved the yields over those reported by Backer and Haack, and carried the synthesis one step further by cleaving the dimethyl ether to obtain the catechol compound.

In view of the current interest in 3-*n*-pentadecylcatechol, because of its possible use as a standard agent for the diagnosis and therapy of poison ivy dermatitis, we are prompted to point out that it was synthesized in our laboratory in minimum over-all yield of 57% from *o*-veratraldehyde over two years ago. The synthesis was not published at that time inasmuch as it was a duplication of the work of Backer and Haack except for the improved yields and the additional ether cleavage step. However, the fact that we had synthesized 3-*n*-pentadecylcatechol was made clear in a later article.[4] Furthermore, the data in this article showing the 100% correlation of hypersensitiveness to poison ivy and to standard acetone solutions of 3-*n*-pentadecylcatechol involving patch tests on 21 patients made obvious the possible use of this synthetic compound as a standard agent for the diagnosis and therapy of poison ivy dermatitis. It would appear that Mason overlooked this article since no reference to it was made in his description of the synthesis nor in his statements in regard to the use of 3-*n*-pentadecylcatechol as a standard allergen.

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(1) Mason, THIS JOURNAL, **67**, 1538 (1945).

(2) Majima and Tahara, *Ber.*, **48**, 1606 (1915).

(3) Backer and Haack, *Rec. trav. chim.*, **57**, 225 (1938).

(4) Keil, Wasserman and Dawson, *J. Exptl. Med.*, **80**, 275 (1944.)