work reported elsewhere,[6] the use of red fuming nitric acid containing urea instead of anhydrous nitric acid gave very low yields of methylenedi-(nitroformamide).

The facile spontaneous hydrolysis of methylenedi-(nitroformamide), even at room temperature, prompted us to investigate the acid hydrolysis of the compound. Calculation of the heat of hydrolysis in the same manner as the heat of nitration[5] shows the evolution of 12 kcal./mole for this reaction. Hydrolysis was investigated in various media including methanol, isopropyl alcohol, water, 2 *N* hydrochloric acid, concentrated hydrochloric acid, 90% formic acid and glacial acetic acid. As methylenedinitramine is most stable in solutions of low *p*H,[4] the best yields are obtained using an acidic medium (methylenedinitramine is unstable in sulfuric acid). The product is contaminated with polymeric solids when hydrolysis takes place in very concentrated solution at *p*H 3-6.

A study of the thermal decomposition of methylenedinitramine has been made and is reported elsewhere.[7]

Experimental

Methylenedi-(nitroformamide).—Absolute nitric acid (19 ml., 0.45 mole) was added at 10–15° dropwise with stirring to a suspension of methylenediformamide (5 g., 0.05 mole) in 19 ml. of acetic anhydride (0.2 mole). The resulting solution was aged for 2 hours at ice temperature and then run into 150 ml. of ice and water with stirring. The precipitate was collected and washed several times by slurrying with ice-water. The product was pressed dry on the filter and then dissolved in 30 ml. of ethyl acetate. The solution was separated from the adhering water and dried over anhydrous sodium sulfate. The ethyl acetate solution was concentrated *in vacuo* to the formation of a precipitate, 10 ml. of isopropyl alcohol was added and the product was collected. The nitroformamide was recrystallized twice by dissolving in 3 ml. of acetone, diluting with 6 ml. of isopropyl alcohol, and then adding 10 ml. of Skellysolve B (it also may be recrystallized from boiling ethylene chloride). The purified product melted at 87–87.5°.

Anal. Calcd. for $C_2H_4O_6N_4$: C, 18.75; H, 2.10. Found: C, 18.76; H, 2.34.

Methylenedinitramine.—Absolute nitric acid (380 ml., 9 moles) was added as rapidly as possible at ±2° (Dry Ice–kerosene cooling) to a well-stirred suspension of 102 g. (1 mole) of methylenediformamide (m.p. 142–143°) in 380 ml. (4 moles) of acetic anhydride. Upon completion of the nitric acid addition, the Dry Ice–kerosene-bath was removed and replaced by an ice-bath, and the mixture allowed to age with ice-cooling for 4 hours. After application of the ice-bath, the temperature of the reaction mixture rose to 8° during 0.25 to 0.5 hour and then fell to +2°, where it remained during the remainder of the aging period. At the end of the aging period, the reaction mixture was run in a stream during 5 minutes into a well-stirred mixture of 500 ml. of water and 1500 g. of finely crushed ice. The precipitate of methylenedi-(nitroformamide) was immediately[8] collected on a filter and washed with three 100-ml. portions of ice-water. The filter cake was pressed dry by use of a rubber dam. The yield at this point was 200 to 300 g. of damp material. The methylenedi-(nitroformamide) was stirred into 105 ml. of 90% formic acid[9] and the resultant paste allowed to hydrolyze[10] by standing overnight. The formic acid and water were removed from the methylenedinitramine by codistillation with xylene.

The recycling xylene azeotropic distillation of formic acid and water was carried out at 25–35° (10–15 mm.) until 1 hour after liquid had ceased to separate from the condensing xylene and the methylenedinitramine had crystallized as a sand. The crude methylenedinitramine[11] was collected on a filter and dried at reduced pressure over paraffin and sodium hydroxide. The yield of material melting at 98–103° was 80–100% based on methylenediformamide.

The crude methylenedinitramine was purified by recrystallization from 2-nitropropane (3 ml./g. at 70–75°) or 9/1 mixture (by volume) of ethylene dichloride and isopropyl alcohol (5 ml./g.). The latter solvent returns 80% in the first crop of crystals. Purified methylenedinitramine melts at 105–106° and decomposes when heated above 110°.

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[6] Private communication from Dr. John Dawson, Rohm and Haas Co.

[7] M. C. Tobin, J. P. Fowler, H. A. Hoffman and C. W. Sauer, This Journal, **76**, 3249 (1954).

[8] Isolation of the methylenedi-(nitroformamide) by precipitation from the reaction mixture in a mixture of ice and water is a very critical point in the procedure. If the temperature of the precipitating solution is allowed to rise above 0°, hydrolysis will take place along with the precipitation and no product will be isolated. This ease of hydrolysis also necessitates rapid separation of the material from the drowning mother liquor, as the yield decreases to less than half on standing for 15 minutes prior to filtration.

[9] An alternate procedure for the hydrolysis of the methylenedi-(nitroformamide) was the following: After the precipitated methylenedi-(nitroformamide) had been collected on the filter, it was washed with three 50–100 ml. portions of ice-cold 2 *N* hydrochloric acid. The dry filter cake (15–25% water) was allowed to hydrolyze without addition of further reagents. The methylenedinitramine was isolated from this hydrolysis solution by either crystallization at −30° or by vacuum azeotropic distillation with xylene.

[10] Hydrolysis of methylenedi-(nitroformamide) produces a solution of methylenedinitramine in the formic acid formed by hydrolysis together with any solvent which had been added. Crystalline methylenedinitramine can best be isolated from this solution either by removal of the solvent (azeotropic distillation) or by low temperature crystallization. Extraction merely gives a second solution from which the compound must still be isolated. Low temperature crystallization was satisfactory when concentrated hydrochloric acid, formic acid, acetic acid, and no solvent other than adherent wash water (2 *N* hydrochloric acid) were used for the hydrolysis.

[11] An alternate procedure for the isolation of methylenedinitramine from the hydrolysis solution was the following: After filtration through acid-hardened filter paper to remove dirt and other insoluble material, the hydrolysis solution was allowed to stand at −30° with intermittent stirring for 8–24 hours. The crystalline methylenedinitramine was collected on a filter and dried *in vacuo* over paraffin and sodium hydroxide. The yield was 62–79% when no solvent was added for hydrolysis and 50–55% when 90% formic acid was added for hydrolysis. Additional methylenedinitramine (20–30%) was obtained from the mother liquor by concentration *in vacuo* to one-quarter volume followed by crystallization at −30°.

Removal of Peroxides from Ethers with Cerous Hydroxide

By J. B. Ramsey and F. T. Aldridge

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In order to obtain readily pure sodium iodide by recrystallization from aqueous solution at room temperature *p*-dioxane has been used to lower the solubility of this salt. Prior to its use for this purpose it is necessary to remove the peroxide found present (*via* the iodide test) in the best grades of *p*-dioxane commercially available. The different methods commonly employed for removing peroxides from ethers were considered and found to have certain undesirable physical or/and chemical features.

It has long been known that cerous hydroxide, an insoluble white solid with somewhat the same texture as ferric hydroxide when precipitated from aqueous solution, reacts quantitatively and readily with hydrogen peroxide in very dilute aqueous solution.[1] This property has been found very useful

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[1] T. Clève, *Bull. soc. chim.*, **43**, 53 (1885).

by Wieland and co-workers[2] in the determination of very small quantities (concentrations) of hydrogen peroxide formed during the oxidation of various organic substances by oxygen in aqueous solution. It seemed probable that cerous hydroxide might react likewise with peroxides present in many ethers.

Recently Moffett and Aspergen[3] reported an unexpected fire which resulted from addition of lithium aluminum hydride to tetrahydrofuran which was presumed to be free from peroxides but shown later to contain them. For removing peroxides from ethers they stress the need and value of having a solid substance which is insoluble and which can therefore be separated from the ether by filtration or decantation. Our results show that cerous hydroxide, Ce(OH)$_3$, fulfills these requirements.

Experimental Procedure and Results

Cerous hydroxide is prepared readily by precipitation from a cerous salt solution (cerous chloride used) by addition of aqueous sodium hydroxide until the supernatant solution is slightly alkaline. The cerous hydroxide (white) is easily removed and washed by centrifugation. The undried cerous hydroxide is used since it is doubtful whether the thoroughly dried hydroxide would react as rapidly with peroxides.

If peroxides are present the cerous hydroxide changes color (from white to reddish-brown) within a minute or two after addition to the ether (30 ml. used). With those ethers which are miscible with water to an appreciable extent the time required to remove the peroxides present (as shown by the iodide test) is in no case greater than 15 minutes. For ethers which are only slightly miscible with water it is necessary to add one or two milliliters of water along with the cerous hydroxide in order to cause complete removal of peroxides in 15 minutes. Otherwise, after partial reaction with peroxides has occurred, the colored precipitate becomes agglomerated in such a way as to prevent rapid reaction between the cerous hydroxide and the peroxides remaining. When water is not added in these cases from three to four hours are required for complete peroxide removal. Incidentally, the use of starch–iodide paper in testing for the presence of peroxides in ethers is not as reliable as a slightly acidified solution of potassium iodide containing starch.

The peroxyceric compound and unchanged cerous hydroxide is removed from the ether by centrifugation and decantation. The cerium present in this mixture may be recovered as cerous cerium, Ce^{III}, by simply dissolving in hydrochloric acid and reducing the Ce^{IV} present to Ce^{III} by addition of the required amount of "Superoxol" (30% hydrogen peroxide), which is shown by the disappearance of the yellow color of Ce^{IV}. Heating gently for a short time assures complete removal of excess hydrogen peroxide. Cerous hydroxide is slowly oxidized by oxygen of the air and if it is to be kept for considerable time it should be stored in an air-tight container. An evacuated desiccator, containing no desiccant, has been found quite satisfactory. In general there should be no need for storage since it is so easily prepared when needed.

After the removal of the peroxides the ethers are tested for the presence of cerium by the benzidine test.[4] The limiting quantity of cerium (as Ce^{III} or Ce^{IV}) identifiable by this test is reported to be $0.18\ \gamma$ and the limiting concentration, 1 part in 275,000. Of the nineteen ethers used only allyl ethyl ether and benzyl *n*-butyl ether gave a positive test for cerium; the latter very slightly positive and the former, strongly positive. The allyl ethyl ether was distinctly yellow, thus indicating the presence of considerable cerium. This may be attributable to the formation of a complex between ceric cerium and this ether (due to the presence of an active double bond), thereby forming a cerium compound which is appreciably soluble in the ether.

The ethers tested (listed below) were of the highest grade commercially available. The quantities of peroxide found present, as indicated by the iodine liberated in the iodide test (2 ml. of the ether +5 ml. of acidified potassium iodide solution +1 ml. of starch solution), are designated by 0 for none, + for very small, ++ for moderate and +++ for considerable or large.

Allyl ethyl ether, ++
Allyl phenyl ether, ++
Benzyl ether, ++
Benzyl *n*-butyl ether, ++
o-Bromophenetole, +
p-Bromophenetole, 0
n-Butyl ether, ++
t-Butyl ether, ++
p-Chloroanisole, 0
o-Chlorophenetole, 0
Diethylene glycol diethyl ether, +++
Diethylene glycol mono-*n*-butyl ether, ++
p-Dioxane, ++
Ethyl ether,[a] 0
Ethyl ether,[b] +++
Ethyl ether,[c] ++
Isopropyl ether, +++
o-Methylanisole, 0
m-Methylphenetole, 0
Phenetole, 0
Tetrahydrofuran, ++

[a] Obtained from sealed tin can of anhydrous ether, analytical reagent, immediately after opening. [b] Obtained from a partially filled tin can (well-stoppered) containing the same grade of anhydrous ether, originally, as that described in note *a*, but of long standing. [c] From a galvanized iron container used for dispensing ether from stockroom for research purposes.

After treatment with cerous hydroxide each of the peroxide-containing ethers, listed above, gives a negative test for peroxide. Also the benzidine test for cerium in the resulting peroxide-free ether was negative in every case with the exception of the two discussed above.

It may be of interest to note that di-*t*-butyl peroxide does not liberate iodine from acidified potassium iodide solution nor does it react with cerous hydroxide. The peroxides found present in *t*-butyl ether are, therefore, other more reactive peroxides.

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[2] H. Wieland and B. Rosenfeld, *Ann.*, **477**, 32 (1929).

[3] R. B. Moffett and B. D. Aspergen, *Chem. Eng. News*, **32**, 4328 (1954).

[4] F. Feigl, "Qualitative Analysis by Spot Tests," 3rd Ed., translated by R. E. Oesper, Elsevier Publ. Co., New York, N. Y., 1946, p. 161.

Phenylglyoxylates of Steroid Alcohols[1]

BY HANS REICH[2]

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Steroid ketones can be converted readily to 2,4-dinitrophenylhydrazones and estimated spectrophotometrically. If a similar method could be found for steroid alcohols, it would facilitate their estimation in biological material and incubation mixtures. It would require first the formation of a keto acid ester, for instance a *d*-camphor 10-sulfonate. Such an ester was prepared from cholesterol, but it was found that it gave only a poor yield of a 2,4-dinitrophenylhydrazone due to the fact that the keto group in camphor is rather unreactive. Better results were obtained with the phenylglyoxylic acid esters of cholestane-3β-ol[3,4] and cholesterol which can be prepared readily in good yield. They reacted quantitatively with dinitrophenylhydrazine in a mixture of ethanol and chloroform containing a small amount of hydrochloric acid. Under the same conditions dehydroepiandrosteryl phen-

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[2] Biochemistry Department, College of Agriculture, University of Wisconsin, Madison, Wis.

[3] W. G. Dauben, D. F. Dickel, O. Jeger and V. Prelog, *Helv. Chim. Acta*, **36**, 325 (1953).

[4] This material was kindly supplied by Dr. V. Prelog, Zurich, Switzerland.