had been consumed, 0.03 mole of alkali utilized, and 0.005 mole of oxygen evolved. After chilling thoroughly, the insoluble solid was collected by filtration, washed with methanol, and dried to a constant weight of 8.2 g., m.p. 202–203°.

By diluting the filtrate with two volumes of water, there was obtained an additional 7.3 g. of crude epoxy amide. Recrystallization from chloroform afforded 1.9 g. of product, m.p. 201–202°. Another crop of 0.4 g., m.p. 195–200°, was secured by dilution with hexane. The total yield of epoxyamide was therefore 10.5 g., or 60%. No further crystalline product was obtained by re-working the filtrate from the last crop.

Attempted epoxidation of α-phenyl-trans-cinnamamide by acetonitrile–hydrogen peroxide. A solution of 5.0 g. (0.0224 mole) of α-phenyl-*trans*-cinnamamide, 5 ml. of acetonitrile, and 3.4 g. (0.050 mole) of 50% hydrogen peroxide in 50 ml. of methanol was stirred magnetically using a large tap water bath for cooling. One milliliter of *N* sodium hydroxide was added to bring the *p*H to 8 and initiate reaction. Three additional 1-ml. portions were added at hourly intervals to maintain the desired *p*H. Oxygen was collected by means of an inverted graduate cylinder. At the end of 2 hr., 185 ml. of gas had been collected and iodometric titration showed that 0.020 mole of peroxide had been consumed. At the end of 4 hr., 245 ml. of gas had been evolved and 0.033 mole of peroxide consumed.

Dilution of the stirred mixture with 150 ml. of water gave crystalline material which was isolated by filtration. It weighed 4.2 g. and had m.p. 115–122°; a mixed m.p. with starting material was 122–127°. The infrared spectrum was virtually identical with that of the starting material. Lack of absorption at 11.00 and 11.31μ indicated the absence of any significant amount of epoxyamide.

A 2.0-g. sample of product was recrystallized from 100 ml. of ether to give 1.4 g. of recovered starting material, m.p. and mixed m.p. 126–128°.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

Reactions of Hydrogen Peroxide. VII. Alkali-Catalyzed Epoxidation and Oxidation Using a Nitrile as Co-reactant

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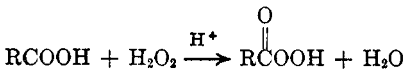
A new epoxidation and oxidation technique has been discovered in which dilute hydrogen peroxide (30–50%) is utilized under essentially neutral conditions. The procedure involves the initial reaction of an organic nitrile with hydrogen peroxide to produce what is most likely a peroxycarboximidic acid. This has been used to epoxidize cyclohexene, styrene, and acrolein diethyl acetal in 73, 70, and 62% yields, respectively, as well as to oxidize pyridine to its *N*-oxide in 79% yield and aniline to azoxybenzene in 62% yield.

Hydrogen peroxide by itself is a relatively poor oxidizing agent. For example, its use in organic reactions has generally been limited to the conversion of tertiary amines to their oxides and sulfides to sulfoxides[1]:

$$R_3N + H_2O_2 \longrightarrow R_3N \rightarrow O + H_2O$$

$$R{-}\underset{\underset{O}{\downarrow}}{S}{-}R' \text{ (from) } R{-}S{-}R' + H_2O_2 \longrightarrow R{-}\underset{\underset{O}{\downarrow}}{S}{-}R' + H_2O$$

For other oxidations, including epoxidation and hydroxylation, the hydrogen peroxide must be "activated" by conversion to another species, usually a peroxy acid (I)[2] or the perhydroxyl anion (II).[3a,b]



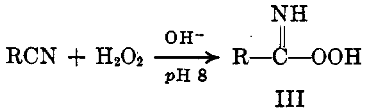
$$RCOOH + H_2O_2 \xrightarrow{H^+} R\overset{O}{\overset{\|}{C}}OOH + H_2O$$

I

$$H_2O_2 + OH^- \longrightarrow H_2O + OOH^-$$

II

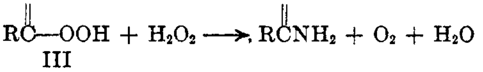
A completely new method of achieving oxidation by hydrogen peroxide was developed through consideration of possible mechanisms involved in the epoxidation of acrylonitrile.[4] In this system, hydrogen peroxide reacts with a nitrile under controlled *p*H conditions (usually *p*H 8) to generate what is felt to be a *peroxycarboximidic acid* intermediate (III). The latter has not been isolated; it reacts rapidly with any available reducing agent. In the absence of an added substrate (an olefin, for example), III reacts with hydrogen peroxide (now acting as the reducing agent) to give amide and oxygen[5]:



$$RCN + H_2O_2 \xrightarrow[pH\ 8]{OH^-} R{-}\overset{NH}{\overset{\|}{C}}{-}OOH \qquad (1)$$

III

$$\text{III} + \text{Reductant} \longrightarrow R\overset{O}{\overset{\|}{C}}NH_2 + \text{Oxidation product} \qquad (2)$$



$$R\overset{NH}{\overset{\|}{C}}{-}OOH + H_2O_2 \longrightarrow R\overset{O}{\overset{\|}{C}}NH_2 + O_2 + H_2O \qquad (3)$$

III

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[1] Reactions of hydrogen peroxide in organic chemistry are summarized by W. C. Schumb, C. N. Satterfield, and R. L. Wentworth in *Hydrogen Peroxide,* Reinhold Publishing Corp., New York, 1955, p. 406.

[2] D. Swern, *Org. Reactions,* VII, 378 (1953).

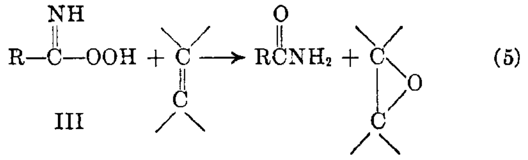
[3] (a) R. C. Elderfield, *Heterocyclic Compounds,* Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 6. (b) See G. B. Payne, *Hydrogen Peroxide: New Techniques for Its Utilization,* Fifth World Petroleum Congress, May 30–June 5, 1959, New York, N. Y., Section IV—Paper 16, for a recent review with references.

[4] G. B. Payne and P. H. Williams, *J. Org. Chem.,* **26,** 651 (1961).

By adding together equations (1) and (3) one arrives at the classical expression for the hydrolysis of an organic nitrile by alkaline hydrogen peroxide ("Radziszewski reaction")[6]:

$$RCN + 2H_2O_2 \xrightarrow{OH^-} R\overset{O}{\overset{\|}{C}}NH_2 + H_2O + O_2 \qquad (4)$$

In the presence of a better reducing agent (the olefin, for example), reaction of III with hydrogen peroxide may often be eliminated and epoxidation of the olefin accomplished instead.



III (5)

It will be noted, of course, that regardless of how III reacts (path 3 or path 5), it is always converted to amide.

The reaction is not limited to epoxidation of ethylenic compounds. Using acetonitrile, for example, aniline was oxidized to azoxybenzene and pyridine to its *N*-oxide.

Epoxidation of cyclohexene by acetonitrile–hydrogen peroxide. Cyclohexene was chosen as a model compound with which to study briefly the new epoxidation procedure. Acetonitrile, because of its moderate reactivity and general availability, was selected as the appropriate co-reactant for hydrogen peroxide. All reactions were carried out in methanol; this is an excellent solubilizing agent for water-soluble and water-insoluble materials.

On the basis of results obtained, certain conclusions were drawn regarding method of operation:

(a) *Optimum pH* is 7.5–8. At higher *p*H, oxygen evolution (measured by wet test meter) increased, indicating an increase in hydrogen peroxide oxidation (Equation 3). Needless to say, this led to a lower yield of epoxide.

(b) *Method of addition.* Hydrogen peroxide was best added slowly to an excess of both nitrile and olefin. This led to higher yields of epoxide, since reaction 2 was promoted at the expense of reaction 3.

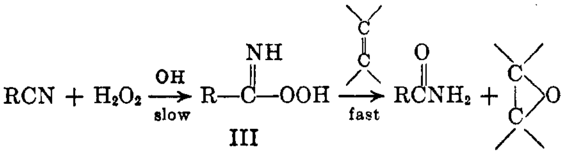
(c) *Temperature.* This was not critical as long as proper *p*H, method of addition, and ratios of reactants were observed. Thus, equivalent yields (80–85% by titration of reaction mixtures for oxirane oxygen) were secured at 60° as well as at 35°.

Epoxidation of cyclohexene using benzonitrile. Benzonitrile was used in place of acetonitrile for the epoxidation of cyclohexene. It was found to be approximately ten times as reactive, and provided an 80% (titrated) yield of 1,2-epoxycyclohexene in six hours at 35°. The yield of distilled epoxy compound was 73%. In another experiment, carried out in a similar manner, crystalline benzamide was also secured in 82% yield.

As a check on the accuracy of measurement of oxygen evolution by the wet test meter, equimolar quantities of benzonitrile and hydrogen peroxide were allowed to react in the absence of cyclohexene. Benzamide was obtained in 94% yield based on peroxide charged, and the amount of oxygen evolved was 97% of theoretical for the quantity of amide isolated.

Epoxidation using trichloroacetonitrile. In order to determine the effect of α-electronegative atoms on the reactivity of the cyano group toward alkaline hydrogen peroxide, trichloroacetonitrile was selected for reaction with cyclohexene. As was expected, the reaction proceeded rapidly at a *p*H approximately 2–3 units lower than usual to give 1,2-epoxycyclohexane in a titrated yield of 52% based on peroxide charged.

Relative rates of epoxidation of 1-hexene and 2-methyl-2-butene. The rate of reaction of a peroxycarboxylic acid with an ethylenic compound is highly dependent upon the degree of substitution at the double bond. For example, 2-methyl-2-butene is epoxidized by peroxyacetic acid at a rate 290 times that of 1-hexene.[7a] In contrast to the above result, the rate of disappearance of hydrogen peroxide in a mixture of acetonitrile, hydrogen peroxide, and olefins is essentially independent of olefin structure. This means that the slow step in the process has to be the formation of the peroxy carboximidic acid intermediate (III); this species must react rapidly with any available reducing agent.



III

Reaction of hydrogen peroxide with acetonitrile in the absence of base. In order to test the reactivity of hydrogen peroxide with acetonitrile in the absence of any added alkali, a solution of the former in the latter was allowed to reflux (68°) for 24 hours in the presence of added cyclohexene. Less than 5% of the peroxide reacted during that extended period.

Epoxidation of other ethylenic compounds. Styrene was epoxidized using acetonitrile in methanol solution at 50° for seven hours. The yield of distilled styrene oxide was 74% based on unrecovered styrene or 70% on the basis of hydrogen peroxide charged.

It was hoped that by operating under almost neutral conditions with the nitrile-peroxide system it would be possible to obtain certain epoxides which could not otherwise be prepared via the usual acidic peroxy acids. For example, *n-butyl vinyl ether* might afford the simple epoxy ether (IV)

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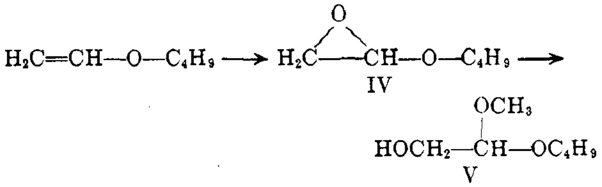
(5) K. B. Wiberg, *J. Am. Chem. Soc.*, **75**, 3961 (1953).

(6) B. Radziszewski, *Ber.*, **17**, 1389 (1884).

(7a) D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947).

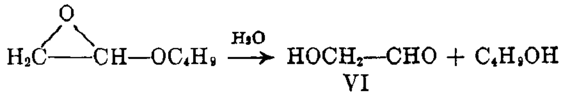
rather than a solvolysis product. Unfortunately, IV was extremely susceptible to solvolysis, even



IV

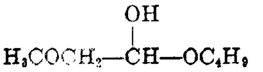
V

near neutrality, and the only product isolated from a reaction carried out in methanol was V (33% yield). The latter arose, of course, by reaction of IV with the methanol solvent. Since there was a considerable amount of water present in the reaction mixture, it seems likely that IV was also converted to the water-soluble product, glycolaldehyde (VI). No attempt was made to isolate any of the latter material.



VI

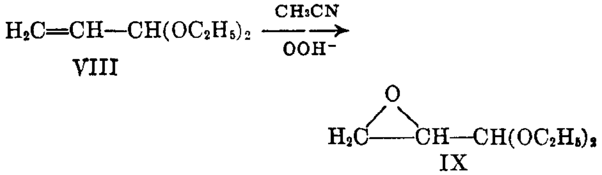
Structure V was established by suitable analyses and by virtue of (1) its conversion to glycolaldehyde *p*-nitrophenylosazone and (2) its reaction with acetic anhydride to give methyl acetate. The latter reaction was carried out to eliminate the (unlikely)[7b] isomeric hemiacetal (VII) as a possible structure for the product; VII would not be expected to give methyl acetate on treatment with acetic anhydride.



$$\mathrm{H_3COCH_2{-}\overset{OH}{\overset{|}{C}}H{-}OC_4H_9}$$

VII

Acrolein diethyl acetal (VIII) was converted to glycidaldehyde diethyl acetal (IX) in 62% distilled yield by the action of acetonitrile and hydrogen peroxide at 50° for six hours.



VIII

IX

In view of the known tendency of acetals to undergo hydrolysis under acidic conditions, it was suspected that the *peroxyacetic acid* oxidation of acrolein diethyl acetal might give an inferior yield. This suspicion was confirmed by a reaction (chloroform solution) which was halted at 85% completion after 48 hours at room temperature. The yield of distilled IX was only 4%, thus indicating a striking advantage for the nitrile method in this case.

Oxidation of amines. Pyridine. A solution of pyridine, benzonitrile, and hydrogen peroxide in methanol solution was observed to have a *p*H of 6.5–7 by indicator paper. In one hour at room temperature there was no consumption of peroxide. When the *p*H was raised to 8, however, an exothermic reaction ensued and cooling was needed to maintain the temperature at 25–30°. At the end of three hours, 95% of the peroxide had been consumed and 4 mole % of oxygen had been evolved. Work-up afforded a 79% yield of pyridine *N*-oxide.

Aniline. Aniline had been oxidized earlier by peroxyacetic acid to give azoxybenzene in moderate yield,[8] and by peroxytrifluoroacetic acid to give nitrobenzene in high yield.[9] It was therefore desirable to determine how this simple aromatic amine would respond to the action of acetonitrile–hydrogen peroxide.

The oxidation was carried out at 50° in methanol solution using acetonitrile and an excess of peroxide. Azoxybenzene was the only product identified; the yield of recrystallized material was 62% based on aniline charged.

EXPERIMENTAL

Epoxidation of cyclohexene by acetonitrile–hydrogen peroxide. The following procedure is typical of the general method of epoxidation by acetonitrile–hydrogen peroxide at 60°.

To a 1-l., five-neck, round-bottom flask equipped with stirrer, thermometer, two dropping funnels, condenser, and *p*H electrodes were charged 300 ml. of methanol, 82 g. (2.0 moles) of acetonitrile (E. K. Co. practical grade) and 123 g. 1.5 moles) of cyclohexene (Phillips pure grade). The mixture was warmed with stirring to 60° and rubber tubing attached to a wet test meter was connected to the top of the condenser. One mole of 50% hydrogen peroxide was added dropwise over a 2-hr. period at 60° ± 2° while 1*N* sodium hydroxide was added simultaneously to maintain an indicated *p*H of 9.5–10. At the end of the peroxide addition, an iodometric titration showed the presence of 0.17 mole of peroxide; titration for oxirane oxygen[10] at the same time indicated the presence of 0.70 mole of cyclohexene oxide (85% yield based on peroxide consumed). After 1.5 hr. longer, only 0.03 mole of peroxide remained and the epoxide formed amounted to 0.80 mole. Less than 0.01 mole of oxygen was evolved during the reaction and the alkali consumption amounted to 0.045 mole.

The mixture was diluted with 500 ml. of water and extracted with three 150-ml. portions of chloroform. After washing and drying, the combined extract was concentrated to a volume of about 150 ml. by means of a 40-tray Oldershaw column. Distillation through a 0.7 × 50 cm. glass spiral-packed column then gave 68 g. (70% based on hydrogen peroxide) of 1,2-epoxycyclohexane, b.p 54–55° (10 mm.); n_D^{20} 1.4525 (lit.,[11] b.p. 129–130°; n_D^{20} 1.4528).

Epoxidation of cyclohexene by benzonitrile–hydrogen peroxide. (A) The following procedure demonstrates epoxidation by benzonitrile–hydrogen peroxide where all of the peroxide is added at the start of the reaction.

To the above setup were charged 400 ml. of methanol, 154.5 g. (1.5 mole) of benzonitrile (b.p. 53–4°/5 mm.; n_D^{20}

[7b] See C. L. Stevens, R. L. McLean, and A. J. Weinheimer, *J. Am. Chem. Soc.*, **80,** 2276 (1958) for a discussion of the alcoholysis of epoxy ethers.

[8] F. P. Greenspan, *Ind. Eng. Chem.*, **39,** 847 (1947).

[9] W. D. Emmons, *J. Am. Chem. Soc.*, **76,** 3470 (1954).

[10] Hydrochloric acid in dioxane; see J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, *Organic Analysis*, Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 135.

[11] C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, **77,** 2549 (1955).

1.5278), 123 g. (1.5 moles) of cyclohexene, and 68 g. (1.0 mole) of 50% hydrogen peroxide. The mixture was stirred at 35–40° with slight cooling as $1N$ sodium hydroxide was added to maintain an indicated pH of 9.5 (true pH ~7.5). After 6 hr., the reaction was 93% complete by titration for peroxide; 0.014 mole of caustic had been consumed and 0.025 mole of oxygen evolved.

Titration for epoxide by hydrochloric acid–dioxane indicated the presence of 0.77 mole of 1,2-epoxycyclohexane (83% yield based on peroxide consumed). No attempt was made to isolate the epoxy compound. Instead, the reaction mixture was concentrated under vacuum to the point where crystallization of benzamide began. The concentrate was diluted with 1 l. of water, chilled, and the solid collected by filtration and washed with water and petroleum ether. The yield of benzamide thus secured was 89 g. (82% based on peroxide consumed), m.p. and mixed m.p. 126–127°.

(B) This procedure illustrates the use of benzonitrile–hydrogen peroxide at 50° with slow addition of peroxide.

To the reaction flask were charged 62 g. (0.75 mole) of cyclohexene, 77 g. (0.75 mole) of benzonitrile and 250 ml. of methanol. With stirring at 50° was added 0.50 mole of 50% hydrogen peroxide over a 2-hr. period. A true pH of 7.5–8 was maintained by the use of $1N$ caustic. One hour after completion of the addition, an iodometric titration indicated the reaction to be 96% complete and a titration for epoxide showed the presence of 0.40 mole of 1,2-epoxycyclohexane (80% yield based on peroxide charged). During the reaction only 0.01 mole of caustic was consumed and a like amount of oxygen evolved.

The mixture was diluted with 500 ml. of water and extracted with three 150-ml. portions of chloroform. After washing and drying, the combined extracts were concentrated to a low volume using a 40-tray Oldershaw column. Chilling of the concentrate allowed the recovery of 30 g. of crystalline benzamide. The filtrate from this operation was then distilled through a 0.7 × 50 cm. glass spiral-packed column to give 36 g. (73% yield) of 1,2-epoxycyclohexane, b.p. 54–56° (50 mm.); n_D^{20} 1.4529.

Epoxidation of cyclohexene by trichloroacetonitrile–hydrogen peroxide. To a 1-l. flask equipped as above were charged 300 ml. of methanol, 57 g. (0.70 mole) of cyclohexene, 97g. (0.68 mole) of trichloroacetonitrile and 34 g. (0.50 mole) of 50% hydrogen peroxide. Since the solution was strongly acidic, about 5 ml. of $3N$ alkali was added to bring the pH to 3–4. At that point, $1N$ caustic was added dropwise to maintain a meter pH of 5–5.5 (true pH ~5) as cooling was required to maintain the temperature at 35°. After 1 hr., the reaction was 83% complete as determined by iodometric titration; in 2 hr., peroxide consumption levelled at 92% completion.

Titration for epoxide by hydrochloric acid in dioxane indicated the presence of 0.26 mole of 1,2-epoxycyclohexane (52% yield based on peroxide charged). Oxygen evolution during the experiment amounted to <0.01 mole; acidic by-product, measured by caustic utilization, was only 3 mole %.

Relative rate study using cyclohexene, 1-hexene, and 2-methyl-2-butene. The following procedure was used with all three of the above unsaturated compounds.

To a 1-l. flask equipped as above were charged 400 ml. of methanol, 62 g. (1.50 moles) of acetonitrile, 1.50 moles of ethylenic compound, and 1.0 mole of 50% hydrogen peroxide. The mixture was stirred at 35° ± 1° while adding $1N$ sodium hydroxide to maintain a meter pH of 9.5 ± 0.1. Iodometric titrations with 20% potassium iodide (20 ml.) in 30% sulfuric acid (100 ml.) were carried out hourly using 1-ml. aliquots.

The following times to 30% reaction were observed: 1-hexene, 3.3 hr.; cyclohexene, 2.6 hr.; 2-methyl-2-butene, 3.3 hr. Straight lines were observed up to 40–50% reaction when $\log_{10}$ (hydrogen peroxide) was plotted against time.

Epoxidation of styrene. Acetonitrile and hydrogen peroxide were used at 50° and pH ~7.5, with the peroxide being added over 2 hr. The reaction was complete in 4 additional hr. to give styrene oxide, b.p. 98–99° (35 mm.) n_D^{20} 1.5348 (lit.,[12] b.p. 188–192°) in 70% yield based on peroxide charged and 74% yield based on unrecovered styrene. The product was isolated by diluting the reaction mixture with water and extracting with chloroform.

When the reaction was carried out at pH 8.5, it was 90% complete in only 2 hr. to give styrene oxide in 42% yield.

Glycidaldehyde diethyl acetal. The procedure used above for styrene was employed with acrolein diethyl acetal (Aldrich, b.p. 121–124°). Work-up by chloroform extraction followed by distillation gave the epoxy acetal in 62% yield based on peroxide charged, b.p. 62–63° (13 mm.); n_D^{20} 1.4140 [lit.,[13] b.p. 60–64° (13 mm.); n_D^{25} 1.4128].

Epoxidation of acrolein diethyl acetal by peracetic acid. A solution of 32 g. (0.25 mole) of unsaturated acetal in 200 ml. of chloroform was treated with 48 g. (0.27 mole) of 42.8% peracetic acid (Becco; 1.0 g. of anhydrous sodium acetate added to neutralize the sulfuric acid present) and the mixture was allowed to stand at room temperature for 2 days. Iodometric titration then indicated that 85% of the theoretical amount of peroxy acid had been consumed.

The mixture was washed with a solution of 50 g. of sodium carbonate in 150 ml. of water and the aqueous solution was back-extracted with 50 ml. of chloroform. The combined chloroform was washed with half-saturated ammonium sulfate solution and dried over magnesium sulfate. Distillation through the glass spiral column gave 1.3 g. (4%) of glycidaldehyde diethyl acetal, b.p. 38–40° (3 mm.); n_D^{20} 1.4157.

2-Methoxy-2-butoxyethanol from n-butyl vinyl ether. To a solution of 150 g. (1.5 moles) of n-butyl vinyl ether and 62 g. (1.5 moles) of acetonitrile in 400 ml. of methanol was added dropwise over 2 hr. at 35° 1 mole of 50% hydrogen peroxide. The meter pH was held at 9.5–10.0 by $3N$ caustic. After 6 hr., 0.16 mole of peroxide remained; 0.19 equivalent of caustic had been consumed, but only 0.01 mole of oxygen was evolved. Titration for oxirane oxygen indicated the possible presence of 0.10 mole of 2-butoxyoxirane.

After dilution of the reaction mixture with 1 l. of water, it was extracted with seven 200-ml. portions of ether. The combined ether, after washing with 100 ml. of water, drying over magnesium sulfate, and concentrating on the steam bath, was distilled through a 0.7 × 50 cm. glass spiral-packed column to give 49 g. (33% yield based on peroxide charged) of 2-methoxy-2-butoxyethanol, b.p. 75–76° (5 mm.); n_D^{20} 1.4227.

Anal. Calcd. for $C_7H_{16}O_3$: C, 56.7; H, 10.9; hydroxyl value, 0.68 equiv./100 g. Found: C, 56.7; H, 10.9; hydroxyl value, 0.68 equiv./100 g. (lithium aluminum hydride).

Treatment of a sample of the acetal with p-nitrophenylhydrazine in acidic ethanol solution led to the formation of *glyoxal p-nitrophenyl osazone*, m.p. 306–307° dec.[14] after recrystallization from pyridine; mixed melting point with an authentic osazone freshly prepared from 30% aqueous glyoxal solution was not depressed.

A mixture of 15 g. (0.1 mole) of the acetal, 41 g. (0.40 mole) of acetic anhydride and 1.0 g. of p-toluenesulfonic acid was allowed to distill through the spiral-packed column to give 3 ml. of methyl acetate, b.p. 57–58° n_D^{20} 1.3610 (lit.,[15] b.p. 57.5°, n_D^{20} 1.3593).

Pyridine N-oxide. To a 1-l. flask equipped as above were charged 400 ml. of methanol, 1.5 moles of pyridine, 1.5 moles of benzonitrile, and 1.0 mole of 50% hydrogen peroxide. Since no reaction occurred at the existing pH (6.5–

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[12] H. Hibbert and P. Burt, *J. Am. Chem. Soc.*, **47**, 2240 (1925).

[13] D. I. Weisblat, B. J. Magerlein, D. R. Myers, A. R. Hanze, E. I. Fairburn, and S. T. Rolfson, *J. Am. Chem. Soc.*, **75**, 5893 (1953).

[14] N. A. Milas, S. Sussman, H. S. Mason, *J. Am. Chem. Soc.*, **61**, 1884 (1939) report m.p. 306–307° for derivative prepared from glycolaldehyde.

[15] I. Heilbron, *Dictionary of Organic Compounds*, Vol. 3, Oxford University Press, New York, 1953, p. 286.

7), a 10-ml. portion of 0.1N sodium hydroxide was added to raise the pH to about 8. An exothermic reaction developed and slight cooling was needed to maintain the temperature at 25–30°. At the end of 3 hr., 95% of the peroxide had been consumed; 0.04 mole of oxygen had been evolved.

After concentration under vacuum at 60° and 5 mm. (final pressure), the residue was diluted with chloroform, chilled, and the crude benzamide (83 g., m.p. 120–125°) collected by filtration. Reconcentration of the filtrate followed by Claisen distillation gave 86 g. of crude pyridine N-oxide, b.p. 90–100° (<1 mm.), contaminated with a small amount of benzamide. The latter was removed by dissolving the crude N-oxide in water and chilling to precipitate 8 g. The aqueous filtrate was extracted with chloroform, concentrated under vacuum, and Claisen-distilled to give 75 g. (79% yield based on hydrogen peroxide) of purified pyridine N-oxide, b.p. 115–120° (5 mm.) [lit.,[16] b.p. 138–140° (15 mm.)]; the product crystallized to a solid white mass.

Anal. Calcd. for C_5H_5NO: C, 63.1; H, 5.3. Found: C, 62.7; H, 5.6.

Oxidation of aniline. To a stirred solution of 18.6 g. (0.20 mole) of freshly distilled aniline and 41 g. (1.0 mole) of acetonitrile in 300 ml. of methanol held at 50° was added 0.60 mole of 50% hydrogen peroxide over a 1-hr. period. The true pH of about 8 was maintained by the addition of 1N sodium hydroxide, the meter pH was 9.5. After an additional 3 hr., iodometric titration indicated the presence of 0.26 mole of peroxide. No oxygen was evolved. Palladium on charcoal catalyst was added to decompose the excess peroxide during an overnight stand in the refrigerator. After filtration, followed by concentration under vacuum to a volume of 75 ml., the residue was extracted with ether. The ether extract was washed, dried, and concentrated to a constant weight of 18 g. Recrystallization from a small volume of acetone–petroleum ether (b.p. 30–60°) afforded 12.3 g. (62% yield) of azoxybenzene, m.p. and mixed m.p. 34–35°.

Reaction of benzonitrile with hydrogen peroxide in the absence of added substrate. A solution of 51.6 g. (0.50 mole) of benzonitrile and 34.0 g. (0.50 mole) of 50.1% hydrogen peroxide in 250 ml. of methanol was stirred at 35° ± 2° while 1.09N sodium hydroxide was added to maintain a *meter* pH of 9.3–9.5. After 1.5 hr. the reaction was 64% complete by iodometric titration and the pH was then held at 9.7–9.9. At the end of 4 hr. total time, the reaction was 94% complete. After an overnight stand at room temperature without further alkali addition, it was 98% complete. Oxygen evolution, as measured by a calibrated wet test meter, amounted to 0.228 mole. Sodium hydroxide consumption was 32 ml. or 0.035 mole.

In order to recover benzamide quantitatively, the reaction mixture was concentrated under vacuum to a dry residue. This was boiled with chloroform, and insoluble material was removed by filtration. Dilution of the filtrate with excess petroleum ether (b.p. 30–60°) caused 28.5 g. (0.235 mole) of benzamide to precipitate; m.p. 126–127°. The yield of amide based on hydrogen peroxide charged was 94%.

EMERYVILLE, CALIF.

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[16] E. Ochiai, *J. Org. Chem.*, 18, 534 (1953).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

Reactions of Hydrogen Peroxide. VIII. Oxidation of Isopropylidenemalononitrile and Ethyl Isopropylidenecyanoacetate

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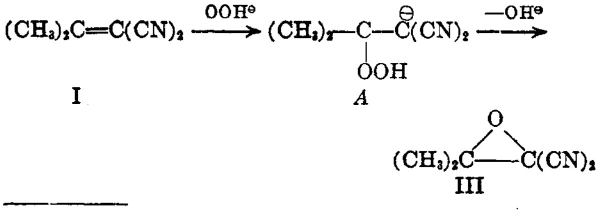
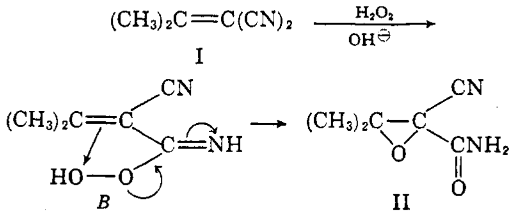
Isopropylidenemalononitrile and ethyl isopropylidenecyanoacetate were found to react readily with hydrogen peroxide under controlled pH conditions to produce substituted epoxyamides as major products. Also isolated were the corresponding epoxydinitrile and α-cyano epoxy ester. Different reaction mechanisms are proposed to account for the two types of products obtained.

In a continuation of studies concerned with the reactions of hydrogen peroxide under controlled pH conditions, isopropylidenemalononitrile (I) and ethyl isopropylidenecyanoacetate (VIII) were selected as materials considered likely to give products other than epoxyamides.[1] It was originally felt, for example, that I would most likely give the simple epoxide (III) *via* the highly resonance-stabilized carbanion *A:*

Isopropylidenemalononitrile. The reaction of I with hydrogen peroxide was carried out in methanol solution by adding dilute sodium hydroxide at such a rate as to require ice bath cooling of the mixture. This occurred at pH 5–6, and the reaction was complete in about one hour at 25°. In the case where 90% hydrogen peroxide was used as oxidant, peroxide consumption amounted to 1.14 moles per mole of dinitrile. Surprisingly, the major product (69% yield) was again[1] found to be an epoxyamide (II). Epoxydinitrile (III) was also secured, but only in 9% yield.





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[1] G. B. Payne and P. H. Williams, *J. Org. Chem.*, 26, 651 (1961).