As usual, the crude salt obtained after removal of the benzene was used in the dimethylformamide alkylation (Table III).

Neither the sodium nor the barium salt of diethyl malonate could be prepared in this way. Much less than the theoretical amount of water was trapped in each case. Indeed, when sodium hydroxide was substituted for potassium hydroxide in the above procedure, the temperature of the refluxing vapors decreased to 72° as a consequence of hydrolysis (benzene-ethanol azeotrope).

Cyanophenylacetaldehyde. To a stirred suspension of 2.6 g. (0.11 mole) of sodium hydride in 40 ml. of dry dimethylformamide was added 11.7 g. (0.1 mole) of phenylacetonitrile over a period of 5–10 min. The temperature was not allowed to exceed 30°. The red solution was stirred at room temperature for 2 days and then allowed to stand without stirring for 3 more days.

The solvent was removed by distillation at the water pump, the red residue was taken up in cold water and acidified with 10 ml. of cold concd. hydrochloric acid. The precipitated greenish yellow oil was taken up in ether, washed with water to neutrality and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave 12 g. of green semisolid product. Trituration with benzene and collection at the filter gave 5.0 g. (34%) of cyanophenylacetaldehyde, m.p. 150–155°. Two recrystallizations from dilute aqueous ethanol gave colorless crystals, m.p. 157–158°, reported[36] m.p. 158°.

Anal. Calcd. for C_9H_7NO: 74.47; H, 4.86. Found: C, 74.25; H, 4.97.

When the above reaction was worked up after only 5 hr., phenylacetonitrile was recovered nearly quantitatively. Also, treatment of diphenylacetonitrile with sodium hydride in dimethylformamide for 1 week under the above conditions led to a complete recovery of starting material.

Reaction of active methylene compounds with sodium hydride in dimethylformamide. In order to determine qualitatively this type of reactivity, the active methylene compounds were added individually to a suspension of sodium hydride (free of mineral oil dispersant) in dimethylformamide. Reactivity was judged as rapid, slow, or negative by the rate of evolution of hydrogen, detectable exothermicity, and rate of color development. The following compounds reacted rapidly at room temperature to give colored solutions (y = yellow r = red, g = green); $CH_3COCH_2COOC_2H_5$(y), $CH_2(COOC_2H_5)_2$ (y), $CH_2(CN)COOC_2H_5$(y), $C_6H_5CH_2CN$(r), $(C_6H_5)_2CHCN$(r), $C_6H_5CH_2COCH_3$(r), $C_6H_5COCH_3$(r), cyclohexanone (y→r), homophthalic anhydride (y), *N*-cyanomethylphthalimide (r), indene (g). Nitromethane reacted rapidly but gave a white precipitate insoluble even in hot dimethylformamide. The following three substances reacted rapidly only in hot (95–100°) dimethylformamide: $(C_6H_5)_2CHCOOC_2H_5$(y), $C_6H_5CH(C_2H_5)COOCH_2CH = CH_2$(g), *o*-nitrotoluene (r). The following reacted slowly even when heated: $CH_3COOC_2H_5$(y), fluorene (r), ethyl *o*-toluate (y). The following gave little or no noticeable evidence of salt formation even when heated: acetonitrile, propionitrile, α-picoline, γ-picoline, quinaldine, diphenylmethane, triphenylmethane, N,N-dimethyldiphenylacetamide, N,N-pentamethylenediphenylmethanesulfonamide. It is interesting to note that on long standing with sodium hydride in dimethylformamide, diphenylmethane gave a bright lavender color which was rapidly discharged on shaking with air.

Acknowledgments. The authors are indebted to Mr. E. F. Shelberg for the microanalyses and to Mr. W. F. Washburn for the infrared spectrum.

NORTH CHICAGO, ILL.

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[36] M. F. Bodroux, *Bull. soc. chim. France*, [4] **7**, 848 (1910).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

Reactions of Hydrogen Peroxide. VI. Alkaline Epoxidation of Acrylonitrile

GEORGE B. PAYNE AND PAUL H. WILLIAMS

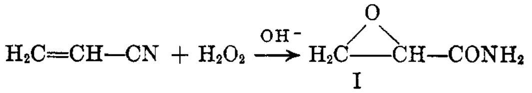
Received April 20, 1960

Reaction of equimolar quantities of acrylonitrile and hydrogen peroxide at *p*H 7.0–7.5 gave glycidamide, a new epoxyamide, in 65–70% yield by titration for oxirane oxygen. An intramolecular rearrangement of peroxyacrylimidic acid is proposed to account for the stoichiometry observed. Evidence for peroxyacrylimidic acid as an intermediate was secured when added cyclohexene underwent epoxidation. α-Phenyl-*trans*-cinnamonitrile, on treatment with alkaline hydrogen peroxide, gave a mixture which included as the major product the epoxyamide which would be expected to result from an intramolecular epoxidation.

The successful epoxidation of acrolein[1] and diethyl ethylidenemalonate[2] by means of hydrogen peroxide under conditions of controlled *p*H indicated that α,β-unsaturated nitriles might respond to the same technique to give epoxy*nitriles*. Earlier,[3,4] treatment of aryl-substituted acrylonitriles with excess hydrogen peroxide in the presence of sodium carbonate had resulted in the formation of epoxyamides rather than nitriles.

Acrylonitrile was selected for an initial study of this reaction. It had been treated earlier with hydrogen peroxide under strongly alkaline conditions to give only "resinous products".[3]

When acrylonitrile and hydrogen peroxide were allowed to react in aqueous solution at *p*H 7.0–7.5 and 35°, glycidamide (I) was produced in 65–70% yield as determined by titration of the reaction



$$H_2C{=}CH{-}CN + H_2O_2 \xrightarrow{OH^-} \overset{\overbrace{\quad O \quad}}{H_2C{-}CH}{-}CONH_2$$

I

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[1] G. B. Payne, *J. Am. Chem. Soc.*, **81**, 4901 (1959.)

[2] G. B. Payne, *J. Org. Chem.*, **24**, 2048 (1959).

[3] J. V. Murray and J. B. Cloke, *J. Am. Chem. Soc.*, **56**, 2749 (1934).

[4] E. C. Kornfeld, E. J. Fornefeld, G. B. Kline, M. J. Mann, D. E. Morrison, R. G. Jones, and R. B. Woodward, *J. Am. Chem. Soc.*, **78**, 3087 (1956).

mixture for oxirane oxygen. Little, if any, of the epoxynitrile (glycidonitrile) could have been present, since flash distillation to remove water afforded less than 2 mole % of volatile epoxide.[5] A bromine number on the residue from this flashing operation indicated the presence of 11 mole % of acrylamide, while titration with periodic acid showed 23 mole % of glyceramide to be present. The latter, of course, would result from solvolysis of the epoxide group of I. While neither of these two by-products was isolated in pure condition, acrylamide was, in one experiment, isolated as the Diels-Alder adduct with cyclopentadiene.

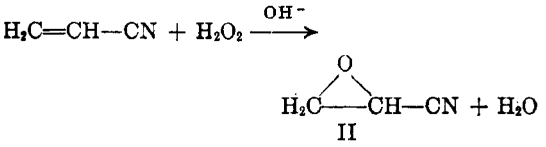
Glycidamide is apparently a new compound, since no reference to it could be found in the chemical literature. Substituted glycidamides are, however, well known and have been prepared in the past from an aryl-substituted unsaturated nitrile by the action of an excess of strongly alkaline hydrogen peroxide,[3] by the peroxy acid epoxidation of an unsaturated amide,[6] from epoxy esters by reaction with ammonia[7-10] and by the interaction of α-chloroacetamide with a ketone.[11,12]

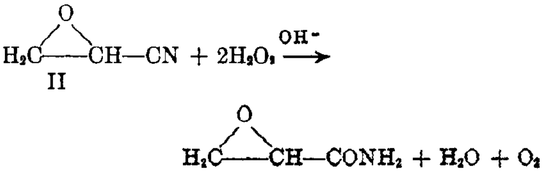
Glycidamide is a very water-soluble, hygroscopic solid melting at 32-34°. One sample was stored in the refrigerator for many months without change in oxirane oxygen content. Another, on heating at 100° for half an hour, suffered a 2.5% loss in oxirane oxygen and became slightly colored.

The epoxyamide was best isolated from the reaction mixture by first removing the solvent water by vacuum flashing below 40° (to minimize hydration of the epoxide linkage); the residue thus obtained was desalted, Claisen-distilled and finally recrystallized. The yield of analytically pure product was 25%. Considerable loss was encountered in the distillation step, presumably through epoxide ring opening by hydroxylic by-products such as glyceramide.

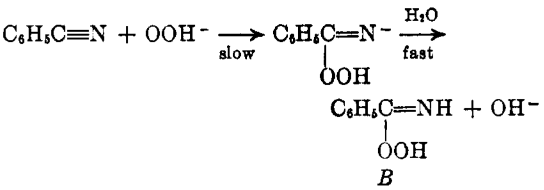
Stoichiometry. Since only one molar equivalent of hydrogen peroxide was consumed when either it or acrylonitrile was in excess, the stoichiometry of the reaction was indicated to be 1:1. Less than 2 mole % of oxygen was evolved.

Lack of oxygen formation, along with the observed stoichiometry, indicated that glycidamide could not have been formed by way of Equations 1 and 2, since that reaction sequence requires the utilization of three moles of peroxide per mole of acrylonitrile as well as the liberation of a molar equivalent of oxygen.[13]

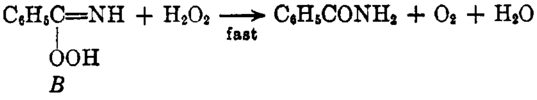

(1)


(2)

Reaction mechanism. Wiberg, in his study of the reaction of benzonitrile with mildly alkaline hydrogen peroxide,[14] found the rate-determining step to be the reaction of peroxide anion with the carbon atom of the nitrile group to give a peroxycarboximidic acid intermediate, *B*. The latter was then felt to oxidize another molecule of hydrogen peroxide by a successive fast reaction.

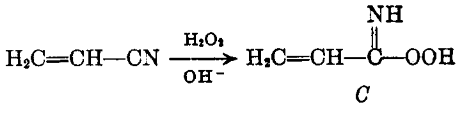


$$C_6H_5C{\equiv}N + OOH^- \xrightarrow[\text{slow}]{} C_6H_5\underset{\substack{|\\ OOH}}{C}{=}N^- \xrightarrow[\text{fast}]{H_2O} \underset{B}{C_6H_5\underset{\substack{|\\ OOH}}{C}{=}NH} + OH^- \quad (3)$$

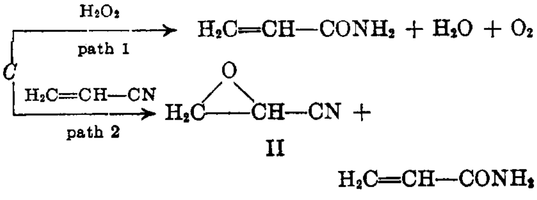


$$\underset{B}{C_6H_5\underset{\substack{|\\ OOH}}{C}{=}NH} + H_2O_2 \xrightarrow[\text{fast}]{} C_6H_5CONH_2 + O_2 + H_2O \quad (4)$$

Consideration of this mechanism for possible application to the acrylonitrile case led to the belief that an intermediate such as *C* might oxidize an ethylenic double bond rather than hydrogen peroxide (path 2 rather than 1). This could lead to the



$$H_2C{=}CH{-}CN \xrightarrow[OH^-]{H_2O_2} \underset{C}{H_2C{=}CH{-}\overset{\substack{NH\\ \|}}{C}{-}OOH} \quad (5)$$


(6)
(7)

formation of an intermediate (II) more reactive toward hydrogen peroxide than acrylonitrile, it-

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[5] Glycidonitrile was recently prepared from glycidaldehyde (ref. 1) and subsequently found to be readily steam-volatile.

[6] R. S. Shelton and K. W. Wheeler, U. S. Patent 2,493,090; *Chem. Abstr.* **44**, 2552 (1950).

[7] V. F. Martynov, Zh. D. Vasyutina, and L. P. Nikulina, *Zhur. Obschei. Khim.*, **26**, 1405 (1956); *Chem. Abstr.*, **50**, 14578 (1956).

[8] F. F. Blicke and J. A. Faust, *J. Am. Chem. Soc.*, **76**, 3156 (1954).

[9] E. Fourneau and R. Billeter, *Bull. soc. chim.*, **7**, 593 (1940).

[10] E. P. Kohler and F. W. Brown, *J. Am. Chem. Soc.*, **55**, 4299 (1933).

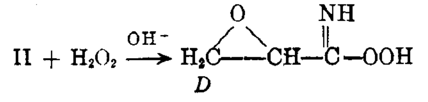
[11] O. von Schickh, *Ber.*, **69B**, 967 (1936).

[12] E. Fourneau, R. Billeter, and D. Bovet, *J. pharm. chim.*, **19**, 49 (1934).

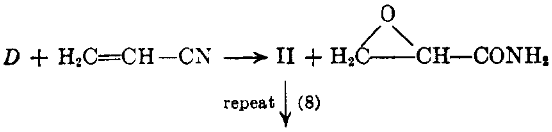
[13] The reaction of a nitrile with alkaline hydrogen peroxide to produce an amide, water, and oxygen is known as a "Radziszewski Reaction;" *Cf.* B. Radziszewski, *Ber.*, **17**, 1289 (1884).

[14] K. B. Wiberg, *J. Am. Chem. Soc.*, **75**, 3961 (1953).

self.[15] A cyclic chain reaction for the formation of glycidamide might then result:



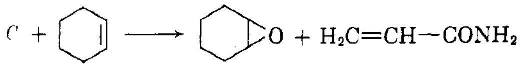
$$\mathrm{II} + H_2O_2 \xrightarrow{OH^-} \underset{D}{H_2\overset{O}{C\text{——}}CH-\overset{NH}{\overset{\|}{C}}-OOH} \quad (8)$$



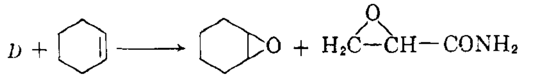
$$D + H_2C{=}CH{-}CN \longrightarrow \mathrm{II} + H_2\overset{O}{C\text{——}}CH{-}CONH_2 \quad (9)$$

$$\downarrow \text{repeat (8)}$$

To gain further information on the mechanism involved, cyclohexene was included in the original system. It was felt that this typical olefin would be a strong enough reducing agent to compete favorably with acrylonitrile for reaction with either *C* or *D:*



(10)



(11)

Results from this experiment did, indeed, show that cyclohexene had been epoxidized. Table I summarizes the yields of products found in the experiments carried out with and without added olefin.

TABLE I

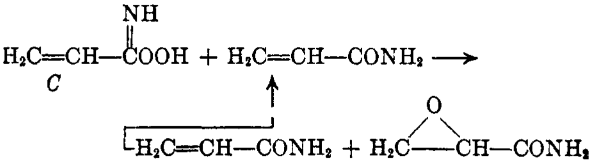
OXIDATION OF ACRYLONITRILE

	Glycidamide[a]	% Yield Cyclohexene Oxide[b]	Acrylamide[c]
Without Cyclohexene	64	—	11
With Cyclohexene	34	23	28

[a] By oxirane oxygen content of residue from flashing. [b] By oxirane oxygen content of flashed material. [c] By bromine number on residue from flashing.

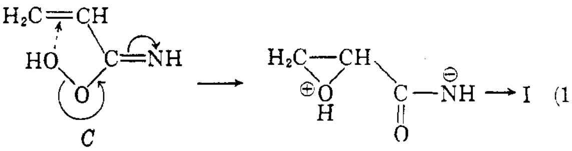
The substantial increase in acrylamide formation[16] was considered significant. It suggested that cyclohexene oxide was being formed by way of Equation 10 (rather than 11) and indicated that the epoxynitrile (II) was probably not an important intermediate in the formation of glycidamide from acrylonitrile. This view was strengthened when it was found that equimolar amounts of acrylonitrile and glycidonitrile reacted with hydrogen peroxide at *p*H 7.5 to give an epoxide yield of only 30%. This, of course, was in marked contrast to the 65–70% yields observed with acrylonitrile alone.

Several mechanisms involving *C* as a key intermediate were considered. Of these, two seemed most reasonable. In the first, acrylamide would be epoxidized intermolecularly by *C* to give glycidamide and another molecule of acrylamide (for further reaction with *C*):



Evidence against this mechanism was secured by carrying out the epoxidation of acrylamide with peroxyacetimidic acid (from acetonitrile–hydrogen peroxide).[17] The 31 mole % of oxygen evolved in that case contrasted sharply with the 2 mole % observed with acrylonitrile.

By the second mechanism, glycidamide would be formed from *C* intramolecularly:.



(12)

The double bond in *C*, no longer strongly polarized by the electron-withdrawing cyano group, might be expected to be more receptive to electrophilic attack than the double bond of acrylonitrile, especially if such attack be intramolecular in nature.[18]

Further evidence in support of an intramolecular mechanism (Equation 12) was secured by investigating the reaction of α-phenyl-*trans*-cinnamonitrile (III) with alkaline hydrogen peroxide. This nitrile was prepared as outlined in Figure 1.

Two possible reaction paths were visualized (Fig. 2). In the first (path 1), peroxide anion adds to the β-carbon to give carbanion IV. This would be expected to rearrange to the more stable con-

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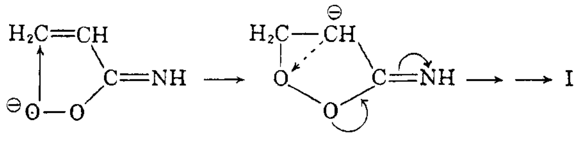
[15] Glycidonitrile (II) was found to react with hydrogen peroxide at approximately 30 times the rate shown by acrylonitrile; in view of the 48 mole % of acidic by-product observed in that case, however, little significance was attached to this figure.

[16] Acrylamide formed in the absence of cyclohexene may have resulted from the reaction of peroxyacrylimidic acid with water:

$$H_2C{=}CH{-}C(NH)OOH + H_2O \longrightarrow H_2C{=}CH{-}CONH_2 + H_2O_2$$

[17] See paper VII in this series for a discussion of epoxidation by acetonitrile–hydrogen peroxide.

[18] One referee suggested that glycidamide might be formed by intramolecular nucleophilic attack:



While this is a possibility, it seems unlikely that an intermediate capable of *electrophilic* attack on cyclohexene (to give the oxide) would also exhibit such nucleophilic character. The electrophilic nature of a peroxyimidic acid intermediate was also demonstrated in the conversion of 2-cyanopyridine to picolinamide *N*-oxide in high yield (see paper IX in this series, *J. Org. Chem.*, **26**, 668 (1961).

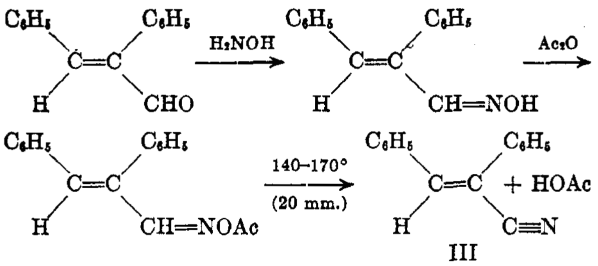


Fig. 1. Preparation of α-phenyl-*trans*-cinnamonitrile

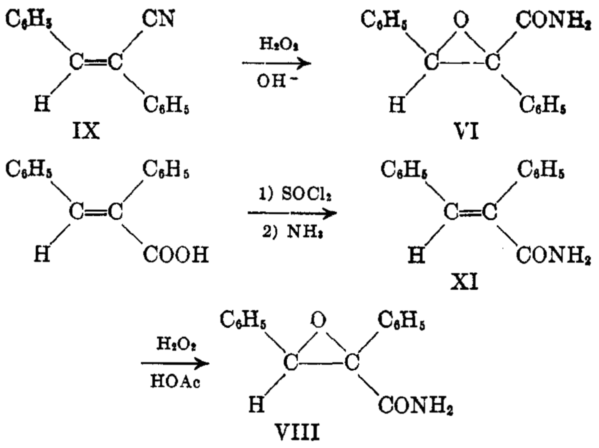


Fig. 3. Preparation of *cis*- and *trans*-epoxyamides

figuration having *trans* phenyls.[19] Displacement of hydroxyl ion would then give the epoxynitrile (V); the latter would hydrolyze to the same epoxyamide (VI) as already obtained from α-phenyl-*cis*-cinnamonitrile (IX).[19]

According to the second mechanism (path 2), epoxidation occurs intramolecularly as detailed above for acrylonitrile (Equation 12). Here there can be no rearrangement and the resulting epoxy amide must have *cis* phenyls.

When III was treated with an excess of strongly alkaline hydrogen peroxide, both epoxyamides (VI and VIII) as well as unsaturated amide (XI) were obtained. These were isolated by fractional crystallization and their structures confirmed by mixed melting points with authentic samples (see Figure 3). In a further experiment to determine more quantitatively the relative amounts of the three products, fractional crystallization and infrared analysis indicated yields of 30, 16, and 10%, respectively, for VIII, VI, and XI.

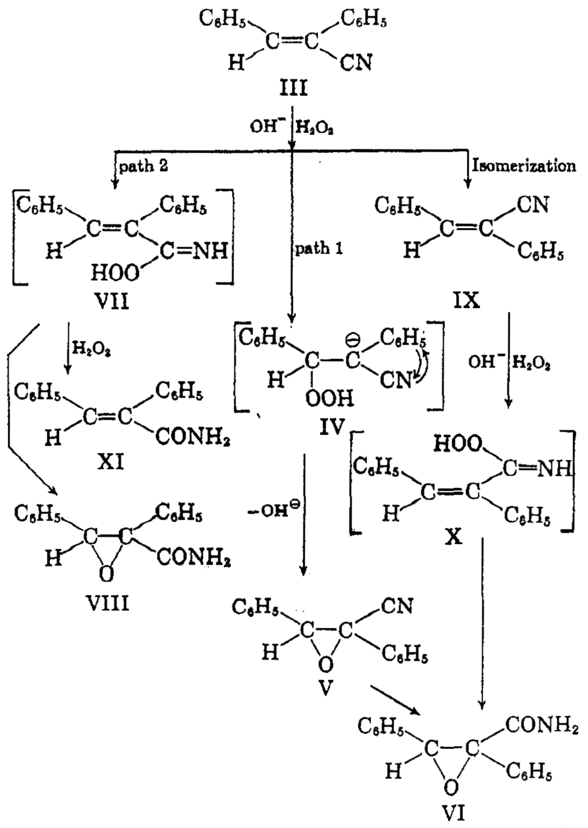
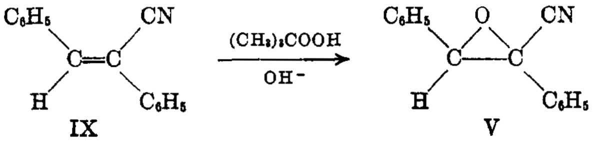


Fig. 2. Reaction of α-phenyl-*trans*-cinnamonitrile with alkaline hydrogen peroxide

The formation of twice as much VIII as VI indicates that path 2 must predominate. Unsaturated amide (XI) was felt to result from the action of hydrogen peroxide on the intermediate peroxycarboximidic acid (VII).[14]

The formation of VI from III need not necessarily occur by path 1; as an alternative, one can postulate a base-catalyzed isomerization of III to IX;[20] the latter could then give VI *via* X.

Epoxynitrile V was desired for a study of its behavior as a possible intermediate in path 1. While alkaline *t*-butyl hydroperoxide[21] reacted with III, no pure product was isolated. However, α-phenyl-*cis*-cinnamonitrile (IX) did give a 76% yield of V on reaction with that hydroperoxide.



Compound V was treated with two molar equivalents of hydrogen peroxide at a *p*H of 8.5. After two and a half hours at 40°, there was obtained only a 31% conversion to epoxyamide (VI) and a 36% recovery of unchanged V. When cyclohexene was included in the reaction system to provide a reducing agent other than hydrogen peroxide, the yield of epoxyamide increased to 70%:

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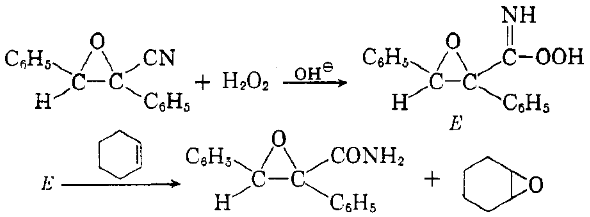
[19] See H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959) for a recent discussion of the stereochemistry of alkaline epoxidation.

[20] III underwent 30% isomerization to IX on standing in 0.1*N* methanolic sodium hydroxide for six hours at room temperature (infrared analysis of the product mixture); under the same conditions, IX was unaffected. A more rapid isomerization of III to IX might be expected in the reaction mixture containing the highly nucleophilic peroxide anion (see reference 14).

[21] N. C. Yang and R. A. Finnegan, *J. Am. Chem. Soc.*, **80**, 5845 (1958); G. B. Payne, *J. Org. Chem.*, **25**, 275 (1960).



This oxidation of cyclohexene indicates that the intermediate peroxyimidic acid (*E*) possesses electrophilic character. In order to operate as an intermediate in the conversion of unsaturated nitrile (IX) to epoxyamide (VI), it would have to undertake electrophilic attack on a conjugated system (*i.e.*, the unsaturated nitrile). Since electrophilic attack (by acetonitrile–hydrogen peroxide[17]) on the α,β-unsaturated amide (XI) was found to be negligible, it seems reasonable to conclude that the α,β-unsaturated nitrile would be even less receptive to this type of attack.[21a]

EXPERIMENTAL[22]

Reaction of acrylonitrile with hydrogen peroxide. Procedure A. To a 1-l., five-neck, round-bottom flask equipped with mechanical stirrer, dropping funnel, thermometer, condenser and standard electrodes connected to a Beckman *p*H Meter, were charged 53 g. (1.0 mole) of acrylonitrile, 300 ml. of distilled water, and 1.20 moles of 30% hydrogen peroxide (standardized before use). The mixture was stirred at 35° while *N* sodium hydroxide was added through the dropping funnel as needed to maintain the *p*H at 7.3–7.5. After 5 hr., an iodometric titration indicated the presence of 0.25 mole of hydrogen peroxide (reaction 95% complete); titration for oxirane oxygen[23,24] showed 0.69 mole of that group to be present. The consumption of 70 ml. of alkali indicated that 7 mole % of acidic by-product had been formed. Oxygen evolution, as measured by a wet test meter connected to the top of the condenser, amounted to only 0.012 mole.

The reaction mixture was treated with 100 mg. of 5% palladium on charcoal (to decompose excess peroxide) and stored overnight in the refrigerator. After removal of this catalyst, the mixture was concentrated at 30–40 mm. by means of a circulating evaporator.[25] Titration of the volatile material (467 ml.) for oxirane oxygen indicated the presence of only 0.016 mole of volatile epoxide. The concentrate (175 g.) contained 0.64 mole of epoxide by titration. A duplicate bromine number also indicated the presence of 0.11 mole of acrylamide, while titration for α-glycol (as a measure of glyceramide) by sodium periodate[26] showed 0.23 mole in the concentrate. (Subsequent blank determinations showed that glycidamide reacted neither with bromine nor with periodate.)

A 128-g. portion of the 175 g. of concentrate was used for the isolation of pure glycidamide. This was desalted by dissolving it in three volumes of acetone, drying over 150 g. of magnesium sulfate, and concentrating under vacuum to a colorless liquid weighing 37 g. When attempted crystallization failed, this material was *carefully* Claisen-distilled at 0.2 mm. using an oil bath for heat.[27] Concurrent resinification was indicated by a pot temperature about 5° higher than that of the oil bath; nonetheless, 15.7 g. (25% yield) of glycidamide, b.p. 72–73° (0.2 mm.) was secured It solidified on standing (m.p. 30–33°) and was 96% pure by titration for oxirane oxygen (theory: 18.4; found, 17.6). Material of analytical purity was obtained by recrystallization from a concentrated acetone solution; it was mildly hygroscopic and had m.p. 32–34°.

Anal. Calcd. for $C_3H_5O_2N$: C, 41.4; H, 5.8; N, 16.1; oxirane oxygen, 18.4. Found: C, 41.5; H, 5.9; N, 16.1; oxirane oxygen, 18.4.

Procedure B. The reaction was carried out as above using 500 ml. of water, 69 g. (1.3 moles) of acrylonitrile and 1.0 mole of 30% hydrogen peroxide. After 7 hr. at a meter *p*H of 7.3–7.5, 0.91 mole of peroxide had been consumed; the mixture was allowed to stand overnight at room temperature without further addition of alkali (52 ml. used). Titration for oxirane oxygen then indicated the presence of 0.67 mole of epoxide. Concentration at 10 mm. using a water bath at 40° led to a residue which was stabilized (35° and 2 mm.) at a constant weight of 73 g. The presence of 54 g. (62% yield) of glycidamide was indicated by titration. Volatile material collected in the cold trap was shown to contain 0.33 mole of acrylonitrile by titration for unsaturation.[28]

The 73 g. was shaken with 400 ml. of acetone and 12 g. of insoluble hygroscopic salt was removed by filtration. Concentration then afforded 60 g. of glycidamide having an 81% purity by titration for epoxide. This was recrystallized from 65 ml. of acetone by chilling overnight at −20°. The 16.3 g. (19% yield) of epoxyamide thus obtained melted at 30–33° and was 95% pure by titration.

Stability of glycidamide. A 0.201-g. sample of epoxyamide was placed in a small stoppered test tube and heated by steam for 0.5 hr. The sample was a very pale yellow in color at the end. It was cooled, dissolved in a small amount of water, and titrated for oxirane oxygen (found: 17.9).

Glyceramide. A solution of 1.7 g. of glycidamide in 25 ml. of water containing 200 mg. of 98% formic acid was allowed to warm at 75° for 5 hr. Complete disappearance of the epoxide link was indicated by titration. After concentration *in vacuo* to an oily residue, crystallization from methanol-

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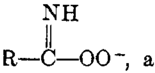
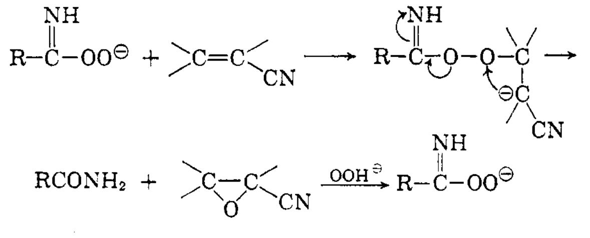
(21a) One referee has suggested a nucleophilic attack on unsaturated nitrile by epoxyperoxyimidate anion,  $R{-}\overset{NH}{\overset{\|}{C}}{-}OO^-$, as a possible route to epoxy amide *via* the epoxynitrile:



This mechanism can, of course, be operative only if the peroxyimidic acid intermediate possesses *both* electrophilic and nucleophilic character. Such a possibility is considered unlikely.

(22) All melting points were taken on an aluminum block using a calibrated thermometer.

(23) Hydrochloric acid in aqueous magnesium chloride; see J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, *Organic Analysis, Vol. 1,* Interscience Publishers, Inc., New York, 1953, p. 134.

(24) All titrations for oxirane oxygen noted in this paper were by hydrochloric acid–magnesium chloride.

(25) D. T. Mitchell, P. Shildneck, and J. Dustin, *Ind. Eng. Chem., Anal. Ed.*, 16, 754 (1944).

(26) Modification of the procedure of V. C. Mehlenbacher, *Organic Analysis, Vol. 1,* Interscience Publishers, Inc., New York, 1953, p. 45.

(27) In another experiment where an acetone desalting was not used, a *violent* polymerization was encountered during distillation.

(28) F. E. Critchfield and J. B. Johnson, *Anal. Chem.*, **28,** 73 (1956).

ether gave 0.7 g. of glyceramide, m.p. 85–86.5°. Recrystallization from a concentrated methanol solution gave 0.3 g., m.p. 89–90° (lit.[29] m.p. 92°).

Anal. Calcd. for $C_3H_7NO_3$: C, 34.3; H, 6.7; N, 13.3. Found: C, 34.1; H, 6.7; N, 13.1.

Reaction of acrylonitrile with hydrogen peroxide in the presence of cyclohexene. Preparative experiment. To a 2-l., five neck flask equipped as above were added 600 ml. of methanol, 123 g. (1.5 moles) of cyclohexene, 53 g. (1.0 mole) of acrylonitrile and 68 g. (1.0 mole) of 50% hydrogen peroxide. This mixture was stirred at 35–40° while 3N sodium hydroxide was added to maintain a *meter* pH of 10.0 ± 0.1 (true pH *ca.* 7.5). After 3 hr., titration indicated the presence of 0.16 mole of peroxide and 0.58 mole of epoxide. One hour later the figures were 0.12 and 0.60, respectively; a total of 0.12 mole of sodium hydroxide had been used and 0.02 mole of oxygen evolved.

The reaction mixture was stored overnight in the cold using palladium on carbon catalyst for decomposition of unchanged peroxide. After filtration, it was flashed at 35° using a circulating evaporator.[28] The volatile material was indicated by titration to contain 0.23 mole of cyclohexene oxide. This product (0.19 mole) was isolated by (1) dilution with water, (2) extraction with methylene chloride, and (3) fractional distillation. It showed b.p. 129–130°, n_{D}^{20} 1.4514 (lit.[30] values: b.p. 129–130°; n_{D}^{20} 1.4528).

Anal. Calcd. for $C_6H_{10}O$: oxirane oxygen, 16.3. Found: 15.7.

Nonvolatile material (154 g.) from the above flashing operation was indicated by titration for oxirane oxygen to contain 0.34 mole of glycidamide. A bromine number indicated the presence of 0.28 mole of acrylamide. Attempted isolation of the latter by fractional crystallization was not successful.

In another experiment, carried out with equimolar amounts of acrylonitrile, cyclohexene, and hydrogen peroxide at a meter pH of 9.5, the reaction was halted after 2 hr. at 82% completion. Mass spectrophotometric analysis of the reaction mixture indicated a relative concentration of 1.23:1, glycidamide to acrylamide. Cyclohexene oxide in the amount of 0.26 mole was indicated by titration of the volatile material for oxirane oxygen. Nonvolatile product contained 0.30 mole of glycidamide by titration; calculated from this latter value, the acrylamide indicated by mass spectrophotometric analysis would amount to 0.25 mole.

Reaction of acrylamide with cyclopentadiene. To a solution of 41 g. (0.58 mole) of acrylamide in 150 ml. of purified dioxane was added 38 g. (0.58 mole) of freshly distilled cyclopentadiene. The mixture was allowed to warm gently on the steam bath, during which time the internal temperature climbed to 90°. After 2 hr. total time, the mixture was cooled and diluted with petroleum ether (b.p. 40–60°). Solid product was collected by filtration and washed well with petroleum ether. It weighed 58 g. (74% yield), m.p. 182–188°.

Recrystallization of 50 g. from 600 ml. of ethanol gave, after cooling to room temperature, 26 g. of relatively pure *endo*-2-norbornene-5-carboxamide, m.p. 196–198°. Two more crystallizations gave the pure *endo* isomer, m.p. 200–201° (lit.[31] m.p. 181–183°).

Anal. Calcd. for $C_8H_{11}NO$: C, 70.1; H, 8.1; N, 10.2. Found: C, 70.4; H, 8.1; N, 10.2.

Hydrogenation was carried out in ethanol solution at room temperature and 50 pounds pressure using 10% palladium on charcoal as catalyst. The product, *endo*-2-norbornanecarboxamide, melted at 208–209° (lit.[32] m.p. 205–206°).

Mother liquor from the recrystallization of 50 g. of mixed isomers (above) was concentrated to one-half volume and cooled to precipitate 8.5 g. of amide, m.p. 182–183°. Concentration of the resulting mother liquor to one-half volume then gave 4.0 g. of amide, m.p. 181–182°. These two crops were combined and recrystallized from 300 ml. of ethanol to give 5.0 g. of *exo*-2-norbornene-5-carboxamide, m.p. 182–183°.

Anal. Calcd. for $C_8H_{11}NO$: C, 70.1; H, 8.1; N, 10.2. Found: C, 70.2; H, 8.1; N, 10.3.

Hydrogenation was carried out as above to give *exo*-2-norbornanecarboxamide, m.p. 191–192° (lit.[32] m.p. 187–188°).

Isolation of acrylamide derivative. To a 2-l., five-neck flask equipped as above were added 800 ml. of methanol, 123 g. (1.5 moles) of cyclohexene, 80 g. (1.5 moles) of acrylonitrile, and 1.00 mole of 50% hydrogen peroxide. The mixture was stirred at 25–30° while 2.96N sodium hydroxide was added to maintain a meter pH of 10.0 (true pH 8 by indicator paper). After 6 hr., iodometric titration showed the reaction to be 75% complete. The solution was allowed to stand overnight without further alkali addition; at that time, 0.11 mole of peroxide remained, no oxygen had been evolved, and 19 ml. (0.056 equiv.) of alkali had been consumed.

Titration of the reaction mixture for oxirane oxygen indicated the presence of 0.71 mole of glycidamide and cyclohexene oxide.

A 20% aliquot of the mixture was treated with 1.0 g. of hydroquinone and pumped at room temperature and a final pressure of 1 mm. to remove all volatile materials including cyclohexene oxide. These were collected in two Dry Ice–acetone cooled traps connected in series, combined, diluted with methanol to give a homogeneous solution, and titrated for oxirane oxygen as a measure of cyclohexene oxide. Found: 0.076 mole. This corresponds to a 38% yield based on hydrogen peroxide charged.

Nonvolatile material from the above operation amounted to 16.5 g.; this included the hydroquinone. It was shaken thoroughly with 50 ml. of ethanol and filtered to remove 1.9 g. of insoluble material, presumably sodium salt and/or polymer. The filtrate was diluted with ethanol to give a volume of 100 ml. A 75-ml. portion of this was treated with 5 g. of freshly distilled cyclopentadiene and allowed to reflux overnight on the steam bath. The resulting dark solution was treated with charcoal and filtered to give an orange solution which, on cooling, readily deposited tan crystalline solid. This weighed 3.8 g. and had m.p. 184–189°; the mixed melting point with an authentic sample of a mixture of *exo*- and *endo*- 2-norbornene-5-carboxamide (prepared in 75% yield from acrylamide and cyclopentadiene by exactly the same procedure; m.p. 188–194°) was 185–191°. Recrystallization from ethanol gave 1.6 g. of pure *endo* isomer, m.p. and mixed m.p. 200–201° (lit.[31] m.p. 181–183°).

Anal. Calcd. for $C_8H_{11}NO$: C, 70.1; H, 8.1. Found: C, 70.0; H, 8.1.

Allowing for the 75% yield observed in the case of authentic acrylamide, the 3.8 g. (0.028 mole) of adduct thus secured indicated that at least 0.25 mole of acrylamide was present in the original reaction mixture.

A bromine number taken on the ethanolic solution of nonvolatile product indicated the presence of 0.32 mole of acrylamide in the original mixture. This value includes a correction for hydroquinone; the latter was determined separately in a blank experiment.

Relative rates of reaction of glycidonitrile and acrylonitrile with hydrogen peroxide. To a 1-l., five-neck, round-bottom flask equipped as above were added 500 ml. of distilled water, 13.8 g. (0.20 mole) of glycidonitrile,[1] and 21.9 g. (0.20 mole) of 31.1% hydrogen peroxide. The temperature was held at 25 ± 1° and the mixture was stirred as N sodium hydroxide was added to maintain a meter pH of 7.4 ± 0.1. Consumption of hydrogen peroxide was followed by iodometric titration of 5-ml. aliquots. At the end of 1 hr., 0.146 mole (73%)

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(29) I. Heilbron, *Dictionary of Organic Compounds*, Vol. 2, Oxford University Press, New York, 1953, p. 608.

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

(31) W. E. Parham, W. T. Hunter, and R. Hanson, *J. Am. Chem. Soc.*, **73**, 5068 (1951).

(32) K. Alder and G. Stein, *Ann.*, **514**, 197 (1934).

of the peroxide had been consumed and 71 ml. (0.071 equiv.) of alkali had been added; less than 0.01 mole of oxygen was evolved. Titration for oxirane oxygen indicated the presence of 0.18 mole of that functional group. In view of the high alkali utilization (48 mole % based on peroxide consumed) in this experiment, no attempt was made to isolate any of the products.

When the experiment was carried out using acrylonitrile in place of glycidonitrile, 25% of the hydrogen peroxide had been consumed at the end of 5 hr. and the reaction was terminated. Since the time to 25% completion was 10 min. in the case of glycidonitrile, an *approximate* relative rate of reaction of 30:1, glycidonitrile to acrylonitrile, was indicated.

Reaction of glycidonitrile in the presence of acrylonitrile To the usual setup were added 500 ml. of water, 13.8 g. (0.20 mole) of glycidonitrile, 10.6 g. (0.20 mole) of acrylonitrile, and 21.9 g. (0.20 mole) of 31.1% hydrogen peroxide. The mixture was stirred at 25° as *N* sodium hydroxide was added to maintain a meter *p*H of 7.3–7.5. At the end of 1 hr., 0.032 mole of peroxide remained (84% complete), only a trace of oxygen had been evolved, 0.046 mole of base had been consumed, and 0.26 mole of epoxide was present as determined by titration for oxirane oxygen.[33] Two hours later, the reaction was 97% complete, 0.052 mole of base consumed, and 0.26 mole of epoxide still present.

The yield of epoxide group, beyond that originally charged as glycidonitrile, was 30%. In view of the high alkali consumption (26 mole %), no attempt was made to isolate product.

Attempted reaction of acrylonitrile with peracetic acid. A solution of 26.5 g. (0.50 mole) of acrylonitrile in 250 ml. of methanol was treated with 0.50 mole of 40% peracetic acid (Becco; sulfuric acid neutralized with sodium acetate prior to use). After standing at room temperature for 6.5 hr., an aliquot was removed for iodometric titration. The titre was exactly the same as that found at the start, thus indicating no reaction.

Attempted reaction of acrylamide with hydrogen peroxide. A solution of 71 g. (1.0 mole) of acrylamide in 300 ml. of water was treated with 1.10 moles of standardized 30% hydrogen peroxide. This was stirred at 35° as *N* sodium hydroxide was added to maintain a meter *p*H of 7.5. After 2.5 hr., iodometric titration indicated the presence of 1.09 moles of peroxide.

When the *p*H was raised to 8.5, oxygen evolution and alkali consumption were significant and the reaction was not pursued further.

Reaction of acrylamide with acetonitrile-hydrogen peroxide. A solution of 25.0 g. (0.352 mole) of acrylamide, 41 g. (1.0 mole) of acetonitrile, and 23.7 g. (0.352 mole) of 50.5% hydrogen peroxide in 250 ml. of water was stirred at 25° while *N* sodium hydroxide was added to maintain a meter *p*H of 8.8–8.9 (true *p*H *ca.* 8 by indicator paper). At the end of 3 hr., 0.064 mole of peroxide remained (82% conversion), 0.19 mole of epoxide was present (as determined by titration for oxirane oxygen) and 1.01 l. of oxygen had been evolved. The latter value corresponds to 0.09 mole of peroxide having been utilized in a Radziszewski reaction. Yield of epoxide based on peroxide converted was 65%; yield of oxygen based on peroxide converted was 31%.

α-Phenyl-trans-cinnamaldehyde. The procedure used was that described in the literature.[34] To a solution of 14 g. of potassium hydroxide in 320 g. of ethanol at 10° was added 180 g. of freshly distilled benzaldehyde. This solution was stirred at 5–10° while 180 g. of phenylacetaldehyde (b.p. 78–79°/10 mm.; n_D^{20} 1.5251) was added over 5 hr. After stirring an additional hour, the mixture was stored at −20° overnight to complete the precipitation of product. Filtration afforded 125 g. (40% yield) of methanol-washed and vacuum-dried α-phenyl-*trans*-cinnamaldehyde, m.p. 94–95° (lit.[34] m.p. 94°).

α-Phenyl-trans-cinnamaldoxime. The 125 g. of product prepared above was dissolved in 500 ml. of warm ethanol and treated with a warm solution of 48 g. of hydroxylamine hydrochloride in 75 ml. of water. This mixture was stirred at 45–50° while a solution of 36 g. of sodium hydroxide in 65 ml. of water was added portionwise. After completion of the addition, the reaction mixture was stirred for 2 hr. while cooling to room temperature. It was poured onto ice, stirred, and saturated with carbon dioxide. The crude moist oxime obtained by filtration was recrystallized from ethanol to give 110 g. (83% yield) of purified oxime, m.p. 164–165°.

α-Phenyl-trans-cinnamonitrile (*III*). A mixture of 40 g. of oxime and 100 g. of acetic anhydride in a 300 ml. distillation kettle were allowed to warm on the steam bath for 0.5 hr. to form the oxime acetate. Claisen distillation was then carried out at 50 mm. to remove acetic acid and excess anhydride. As the kettle temperature rose above 120°, the pressure was lowered to 20 mm. Careful heating caused the oxime acetate to crack at 140–170° and acetic acid slowly distilled. During this operation, the reaction maintained temperature part of the time, and the heating mantle was lowered at one point to prevent too vigorous a reaction. After about 10 min. at 165–170° (0.5 hr. total time at 140–170°) the reaction was complete. The pressure was lowered to 1 mm. and crude product was flashed over fairly rapidly at 120–135°. The weight of colorless nitrile thus obtained was 36 g. (97% yield); it solidified on standing. Recrystallization from ether-hexane (1:4) followed by cooling at −20° gave 31 g. (85% yield) of α-phenyl-*trans*-cinnamonitrile, m.p. 48–48.5° (lit.[35] m.p. 49–51°). Recrystallization did not alter the melting point.

Reaction of α-phenyl-trans-cinnamonitrile (III) *with hydrogen peroxide. (A) At high pH.* To a 500-ml. round-bottom flask equipped with stirrer and thermometer were charged 12.0 g. (0.059 mole) of α-phenyl-*trans*-cinnamonitrile, 200 ml. of methanol, 20 ml. of 30% hydrogen peroxide, and 12 ml. of 20% sodium hydroxide. The mixture was stirred and held at 35–40° for 2 hr. and then chilled for 1 hr. at −20°. Filtration afforded 3.2 g. (22% yield) of 2,3-*trans*-diphenyl-2,3-epoxypropionamide, m.p. and mixed m.p. 202–203° (lit.[19] m.p. 202–204°).

The filtrate was diluted with 600 ml. of water and stirred 0.5 hr. at room temperature prior to cooling and recovery of a second crop. This weighed 7.2 g. and melted *ca.* 90–110°. Recrystallization from ether gave 2.9 g. of crude α-phenyl-*trans*-cinnamamide (XI), m.p. 119–121°. The infrared absorption spectrum of this material was identical with that of an authentic sample (see below) except for absorption at 11.30μ which indicated the presence of an epoxide impurity. Recrystallization of the 2.9 g. from 200 ml. of ether gave 1.3 g. of relatively pure unsaturated amide, m.p. 123.5–124.5°; mixed m.p. with an authentic sample[36] (m.p. 127–128°) was 124–127°.

Filtrate from the separation of 2.9 g. (above) was concentrated to a volume of 40 ml. and chilled at −20° to precipitate 2.5 g. of crude 2,3-*cis*-diphenyl-2,3-epoxypropionamide (VIII), m.p. 95–100°. Two crystallizations from chloroform-pentane at room temperature gave 0.8 g. of pure product, m.p. and mixed m.p. 133–134°[37] (lit.[10] m.p. 124°). See *Anal.* below.

(B) *High pH-determination of yields of isomeric epoxyamides* (VI *and* VIII). A solution of 1.50 g. (7.32 mmoles) of unsaturated nitrile in 25 ml. of methanol was treated with 2.0

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[33] Glycidonitrile was previously shown (ref. 1) to give an oxirane oxygen value in the amount of 95% of theory.

[34] K. Alder, *Ann.*, **586**, 128 (1954).

(35) P. Pfeiffer, I. Engelhardt, and W. Alfuss, *Ann.*, **467**, 158 (1928).

(36) J. F. Codington and E. Mosettig, *J. Org. Chem.*, **17**, 1027 (1952).

(37) This material melted and resolidified when dropped on the hot stage at 124–125°; further recrystallization did not change this behavior.

ml. of 30% hydrogen peroxide and 2.5 ml. of 3*N* sodium hydroxide and stirred magnetically for 2 hr. at ambient temperature (35° max.). After chilling for 2 hr. at −20°, 0.28 g. (16% yield) of 2,3-*trans*-diphenyl-2,3-epoxypropionamide (VI), m.p. 202–203°, was collected by filtration and washed with water. The filtrate was diluted with excess water and the resulting oil extracted into chloroform. After a water wash, the chloroform solution was concentrated to low volume on the steam bath. No further quantity of VI precipitated on standing, so the concentrate was diluted with pentane and stored at −20° to precipitate 0.54 g. of product, m.p. 105–120°. Infrared analysis indicated that this was 90% 2,3-*cis*-diphenyl-2,3-epoxypropionamide (VIII) and 10% α-phenyl-*trans*-cinnamide (XI). Calculation was made from epoxide absorption bands at 11.00μ and 11.31μ.

Filtrate from the isolation of 0.54 g. was concentrated to a residue on the steam bath. This was recrystallized from ether-pentane to give 0.16 g. of material, m.p. 90–110°. Infrared analysis indicated this to be a mixture composed of 24% of *cis*-epoxyamide and 76% of unsaturated amide.

Filtrate from the above isolation was concentrated to an oily residue of constant weight 0.24 g. Infrared analysis indicated the possible presence of some starting material and unsaturated amide as well as the absence of any *cis*-epoxy amide.

From the foregoing can be calculated the approximate yields of the three products obtained:

	% Yield
2,3-*cis*-diphenyl-2,3-epoxypropionamide (VIII)	30
2,3-*trans*-diphenyl-2,3-epoxypropionamide (VI)	16
α-phenyl-*trans*-cinnamide (XI)	10

(C) *At pH 8.5.* To a flask equipped as above for the reaction of acrylonitrile with hydrogen peroxide were charged 15.0 g. (0.073 mole) of α-phenyl-*trans*-cinnamonitrile, 300 ml. of methanol, and 0.088 mole of 30% hydrogen peroxide. The mixture was stirred at 39–40° with a wet test meter connected to the system; 3*N* sodium hydroxide was added as needed to maintain a meter *p*H of 10.4–10.6 (true *p*H *ca.* 8.5 by indicator paper). After 6 hr., iodometric titration indicated the reaction to be 83% complete and the mixture was allowed to stand at room temperature for 15 hr. without further addition of alkali. Titration then indicated that 0.072 mole of peroxide had been consumed, and the *p*H was still about 8. Alkali utilization was 6 ml. (0.02 mole) and only 0.004 mole of oxygen had been evolved.

After chilling in an ice bath for 1 hr., no VI had precipitated, so the mixture was diluted with two volumes of water and extracted with three 100-ml. portions of chloroform. The combined chloroform extract was washed, dried, and concentrated on the steam bath to an internal temperature of 70°. Dilution with hexane, followed by crystallization at room temperature, gave 2.0 g. of a mixture of *cis* and *trans* epoxyamides, m.p. 120–180°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.3; H, 5.5. Found: C, 75.2; H, 5.7.

Recrystallization from chloroform afforded 1.2 g. (7% yield) of 2,3-*trans*-diphenyl-2,3-epoxypropionamide (VI), m.p. 201–202°.

The filtrate from the isolation of 2.0 g. above was diluted with more hexane, warmed to clear, and allowed to cool slowly to room temperature over several hours; cooling at 0° for 1 hr. and then at −20° overnight afforded 2.2 g. of crude 2,3-*cis*-diphenyl-2,3-epoxypropionamide (VIII), m.p. 105–115°. One recrystallization from chloroform-pentane gave 1.2 g. of product with m.p. and mixed m.p. 132–134°. An analytical sample was prepared by crystallization from ether-pentane, m.p. 133–134°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.3; H, 5.5; N, 5.9. Found: C, 75.6; H, 5.6; N, 5.7.

Epoxidation of α-phenyl-trans-cinnamamide (XI) *by hydrogen peroxide in acetic acid.* A solution of 10.0 g. of unsaturated amide (XI)[36] and 25 g. of 50% hydrogen peroxide in 100 g. of acetic acid was allowed to warm on the steam bath at 95° for 2 hr. Dilution with water to cloud, followed by cooling to room temperature gave only oil; this was extracted into chloroform, washed, dried, and concentrated to low volume. Recrystallization from concentrated ether solution at −5° gave 6.2 g. of relatively pure 2,3-*cis*-diphenyl-2,3-epoxypropionamide (VIII), m.p. 125–130°. The infrared spectrum indicated the presence of a small amount of starting material impurity (shoulder at 6.16μ characteristic of the double bond). Two crystallizations from chloroform-pentane gave 3.8 g. (36% yield) of 2,3-*cis*-diphenyl-2,3-epoxypropionamide (VIII), m.p. 133–134°. The infrared spectrum showed typical amide absorption at 2.90, 2.98, 5.91, and 6.36μ as well as epoxide absorption at 11.00 and 11.31μ.

Epoxidation of α-phenyl-cis-cinnamonitrile (IX) *by tert-butyl hydroperoxide.* A solution of 45 g. (0.22 mole) of unsaturated nitrile (IX) in 300 ml. of benzene was cooled to 10° and treated with 0.24 mole of 97% *t*-butyl hydroperoxide[38] and 2 ml. of Triton B catalyst[39] (vacuum-concentrated at room temperature to remove the bulk of methanol solvent prior to addition). The reaction mixture was placed in an ice bath and allowed to warm to room temperature overnight. An iodometric titration indicated the presence of only 0.015 mole of hydroperoxide, so the mixture was washed with water, dried, concentrated to low volume, and the residue recrystallized from ether-hexane to give 37 g. (76% yield) of 2,3-*trans*-diphenyl-2,3-epoxypropionitrile (V), m.p. 70–70.5°.

Rercystallization of 5 g. from concentrated ether solution gave 1.5 g., m.p. and mixed m.p. 70.5–71°.[40]

Anal. Calcd. for $C_{15}H_{11}NO$: C, 81.4; H, 5.0; N, 6.3. Found: C, 81.4; H, 5.0; N, 6.4.

Reaction of 2,3-trans-diphenyl-2,3-epoxypropionitrile (V) *with hydrogen peroxide.* To a solution of 10.0 g. (0.045 mole) of epoxynitrile (V), 10 ml. of water, and 0.10 mole of 30% hydrogen peroxide in 300 ml. of methanol stirred at 40° was added 1*N* sodium hydroxide to maintain a *p*H of 8.5 by indicator paper (meter *p*H 10.2–10.4). After 2.5 hr., 16 ml. (0.016 mole) of alkali had been used, 0.067 mole of peroxide remained, and 0.004 mole of oxygen had been evolved.

The chilled reaction mixture was filtered to give 2.8 g. (27% yield) of 2,3-*trans*-diphenyl-2,3-epoxypropionamide (VI), m.p. 200–201°. The filtrate, on dilution with water, afforded 4.2 g. of starting material, m.p. 72–73°, contaminated with a small amount of epoxyamide. The mixed m.p. with starting material was 71.5–72.5°. An infrared spectrum was identical with that of the starting material except for two small bands at 5.91 and 6.22μ characteristic of the carboxamide group.

Trituration of 3.9 g. of crude recovered starting material with ether at room temperature gave 0.5 g. of insoluble crude epoxy amide, m.p. 185–195°. The weight of recovered starting material was therefore closer to 3.6 g. (36% recovery) and the yield of epoxyamide was calculated as 31%.

When the reaction was carried out in the presence of an added 10 ml. of cyclohexene, the total yield of epoxy amide was 7.6 g. (70%). The first crop weighed 5.9 g. (m.p. 200–201°) and the second 1.7 g. (m.p. 195–198°).

Reaction of α-phenyl-cis-cinnamonitrile (IX) *with hydrogen peroxide at pH 8.5.* The reaction was carried out with α-phenyl-*cis*-cinnamonitrile[41] exactly as described above for the *trans* isomer. At the end of 2.5 hr., 0.081 mole of peroxide

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(38) Prepared by distillation of commercial material through a 10-tray Oldershaw column; b.p. 36–37° (16 mm.).

(39) Triton B (benzyltrimethyl ammonium hydroxide) was a 35% solution in methanol, obtained from Mid-West Laboratories, Inc.

(40) We wish to thank Professor H. E. Zimmerman of the University of Wisconsin for providing us with an authentic sample.

(41) V. Meyer and H. V. Frost, *Ann.*, **250**, 157 (1889).

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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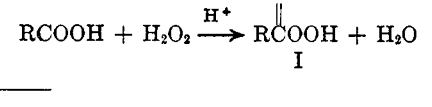
A new epoxidation and oxidation technique has been discovered in which dilute hydrogen peroxide (30–50%) is utilized under essentially neutral conditions. The procedure involves the initial reaction of an organic nitrile with hydrogen peroxide to produce what is most likely a peroxycarboximidic acid. 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.

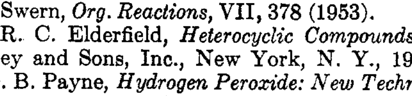
Hydrogen peroxide by itself is a relatively poor oxidizing agent. For example, its use in organic reactions has generally been limited to the conversion of tertiary amines to their oxides and sulfides to sulfoxides[1]:

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



$$R{-}S{-}R' + H_2O_2 \longrightarrow R{-}\underset{\substack{\downarrow\\ O}}{S}{-}R' + H_2O$$

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]



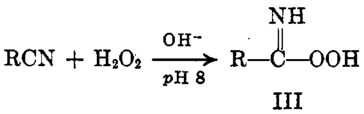
$$RCOOH + H_2O_2 \xrightarrow{H^+} R\overset{O}{\overset{\|}{C}}OOH + H_2O$$

I

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

II

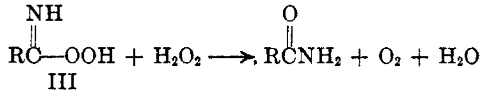
A completely new method of achieving oxidation by hydrogen peroxide was developed through consideration of possible mechanisms involved in the epoxidation of acrylonitrile.[4] In this system, hydrogen peroxide reacts with a nitrile under controlled *p*H conditions (usually *p*H 8) to generate what is 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

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



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

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).