TABLE I[a]

ALKAMINE ESTER HYDROCHLORIDES, $C_6H_5CH(A)COOCH_2$-$C(CH_3)_2NH(B)\cdot HCl$

A	B	Molecular formula	M. p., °C. (uncor.)	Cl analyses, % Calcd.	Found
C_6H_5	n-C_3H_7	$C_{21}H_{28}O_2NCl$	158–159	9.80	9.78
C_6H_5	n-C_4H_9	$C_{22}H_{30}O_2NCl$	173–174	9.43	9.44
C_6H_5	n-C_5H_{11}	$C_{23}H_{32}O_2NCl$	117–118	9.09	9.07
C_6H_5	n-C_6H_{13}	$C_{24}H_{34}O_2NCl$	100–101	8.78	8.75
C_6H_5	i-C_4H_9	$C_{22}H_{30}O_2NCl$	156–157	9.43	9.44
C_6H_5	i-C_5H_{11}	$C_{23}H_{32}O_2NCl$	141–142	9.09	9.12
H	n-C_3H_7	$C_{15}H_{24}O_2NCl$	112–113	12.41	12.61
H	n-C_4H_9	$C_{16}H_{26}O_2NCl$	126–127	11.83	12.00
C_2H_5	n-C_3H_7	$C_{17}H_{28}O_2NCl$	115–116	11.30	11.46
C_2H_5	n-C_4H_9	$C_{18}H_{30}O_2NCl$	109–110	10.81	10.96
C_2H_5	n-C_6H_{13}	$C_{20}H_{34}O_2NCl$	108–109	9.96	10.21

[a] This table contains only the amino alcohol ester hydrochlorides which were readily purified by recrystallization.

A heavy red oil sank from the ether to the bottom of the aqueous layer. A sample of this oil, on being seeded with crystals of a previous preparation of the hydrochloride of β-methyl-β-mono-n-amylaminopropyl diphenylacetate, crystallized within a few minutes. The remainder of the oil and the aqueous layer were made basic with sodium hydroxide solution and extracted with isopropyl ether. Dry hydrogen chloride was passed into the isopropyl ether solution, precipitating a heavy oil, which crystallized within a few minutes, on being seeded. The product, β-methyl-β-mono-n-amylaminopropyl diphenylacetate hydrochloride, was purified by recrystallization from acetone and anhydrous ether.

Summary

A series of hydrochlorides of β-methyl-β-monoalkylaminopropyl phenylacetates, diphenylacetates and phenylalkylacetates is described.

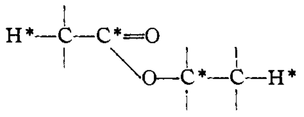
RICHMOND, VA. RECEIVED SEPTEMBER 12, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

β-Elimination and Other Types of Reaction with Certain β-Phenylethyl Esters and Potassium Amide in Liquid Ammonia

BY CHARLES R. HAUSER, JOSEPH C. SHIVERS AND PHILIP S. SKELL

Although the carbonyl carbon or α-hydrogen in the acyl portion of carboxylic esters generally enters into reaction with bases, the α-carbon or β-hydrogen in the alkoxy portion is also capable of reacting. These four vulnerable positions of esters are indicated by asterisks in the following general formula.



Reactions involving the alkoxy portion of esters would be analogous to those exhibited by alkyl halides. Actually several substitutions at the α-carbon, in which the carboxylate group of the ester is replaced by the attacking base, have been observed.[1] β-Elimination, which involves the removal of the β-hydrogen as a proton accompanied by the release of the carboxylate ion to form an olefin,[2] has apparently not been observed with esters of simple aliphatic alcohols, although olefins are produced on pyrolysis of certain of these esters.[3] With esters of alcohols having sufficiently activated β-hydrogens, however, β-elimination is readily effected by bases. β-Nitroethyl acetate, for example, forms nitroethylene even in the presence of bicarbonate.[4]

$$CH_3COO\text{--}CH_2CH_2NO_2 \longrightarrow CH_3COOH + CH_2{=}CHNO_2$$

In the present investigation β-elimination has been realized with certain β-phenylalkyl esters and potassium amide in liquid ammonia.

Although β-phenylethyl benzoate exhibits with potassium amide the carbonyl carbon reaction to form benzamide and β-phenylethyl alcohol, β-phenylethyl mesitoate in which the carbonyl group is hindered undergoes mainly β-elimination to form styrene and mesitoic acid.[5]

$$C_6H_5CO_2CH_2CH_2C_6H_5 \xrightarrow{^-NH_2} C_6H_5CONH_2 + C_6H_5CH_2CH_2OH$$

$$\text{Mes-}CO_2CH_2CH_2C_6H_5 \xrightarrow{^-NH_2} \text{Mes-}COOH + C_6H_5CH{=}CH_2$$

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(1) These include the reaction of methyl benzoate with sodium methoxide to form dimethyl ether [Adickes, *Ber.*, **66**, 1904 (1933); Magnani and McElvain, THIS JOURNAL, **60**, 813 (1938)], the reaction of dimethyl, diethyl or dibutyl phthalate with sodium phenoxide to form the corresponding alkyl phenyl ether [King and Wright, *J. Chem. Soc.*, 1168 (1939)], the reaction of methyl benzoate or acetate with trimethylamine to form the tetramethylammonium ion [Willstätter and Kahn, *Ber.*, **35**, 2757 (1902); Hammett and Pfluger, THIS JOURNAL, **55**, 4079 (1933)], the alkylation of mono-substituted malonic esters with diethyl carbonate to form di-substituted malonic esters [Wallingford and Jones, *ibid.*, **64**, 578 (1942)] and the so-called abnormal acetoacetic ester reaction of benzyl or allyl acetate in the presence of sodium to form the ester of β-phenylpropionic or allylacetic acid [Tseou and Wang, *J. Chinese Chem. Soc.*, **5**, 224 (1937); Bacon, *Am. Chem. J.*, **33**, 68 (1905)]. In the latter reaction the ester anion is assumed to be formed as in the ordinary acetoacetic ester reaction, but, instead of being acylated, it is alkylated by unchanged ester molecules.

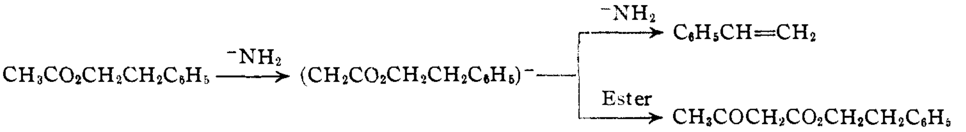
(2) The elimination reaction to form nitriles instead of olefins is common with esters of aldoximes, for example, aldoxime acetates, especially the anti isomers, the reaction being effected by tertiary amines or alkali; see Hauser and Jordan, THIS JOURNAL, **57**, 2450 (1935); Vermillion and Hauser, *ibid.*, **63**, 1227 (1941); Vermillion and Hauser, *J. Org. Chem.*, **6**, 510 (1941).

(3) See Hurd "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, N. Y., 1929, pp. 529–531; Norris and Rigby, THIS JOURNAL, **54**, 2097 (1932).

(4) Schmidt and Rutz, *Ber.*, **61**, 2142 (1928); Hass and Riley, *Chem. Rev.*, **32**, 408, 411 (1943).

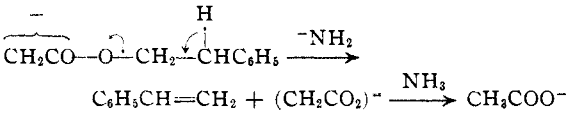
(5) β-Elimination was realized also with β-phenyl-n-butyl mesitoate (b. p. 176° at 3 mm.) but with this ester, in which the β-hydrogen is somewhat deactivated by the β-ethyl group, the carbonyl carbon reaction predominated. With excess potassium amide in liquid ammonia, the products were mesitoamide (60%), mesitoic acid (20%) and an unsaturated neutral substance which appeared to be the olefin

In the presence of two or more equivalents of potassium amide, β-phenylethyl acetate and α,β-diphenylethyl acetate form styrene and stilbene, respectively. With only slightly more than an equivalent of potassium amide, however, β-phenylethyl acetate reacts yet it is recovered on acidification, while, with less than an equivalent of the base, the acetoacetic ester condensation occurs. Evidently, the amide ion first ionizes the α-hydrogen of β-phenylethyl acetate (or α,β-diphenylethyl acetate) to form the ester anion, which undergoes β-elimination with excess amide ion and the condensation with excess ester.[6]



$$CH_3CO_2CH_2CH_2C_6H_5 \xrightarrow{^-NH_2} (CH_2CO_2CH_2CH_2C_6H_5)^- \begin{cases} \xrightarrow{^-NH_2} C_6H_5CH{=}CH_2 \\ \xrightarrow{\text{Ester}} CH_3COCH_2CO_2CH_2CH_2C_6H_5 \end{cases}$$

Apparently, in this β-elimination, the removal of the β-hydrogen is accompanied by the release of the doubly charged acetate ion, which acquires a proton from the medium to form the ordinary acetate ion.[7] It should be pointed out that, in the neutral β-phenylethyl acetate molecule, the carbonyl carbon is probably the second most reactive position, and that β-elimination is realized only because the reactivity of the carbonyl carbon is first largely destroyed by conversion to the ester anion. Although the reactivity of the β-hydrogen also is probably decreased by conversion to ester anion, the effect on this position is much less and β-elimination predominates. With β-phenylethylbenzoate, which has no α-hydrogen, only the carbonyl carbon reaction occurs even though the reactivity of the carbonyl carbon is probably less in the benzoate than in the neutral acetate molecule.[8] Apparently, in the neutral ester molecules the relative reactivities of the four vulnerable positions in β-phenylethyl acetate, and of the three positions in β-phenylethyl benzoate, toward the amide ion decrease in the following order: α-Hydrogen > Carbonyl Carbon > β-Hydrogen > α-Carbon. It should be mentioned that substitution at the α-carbon to form the amine was realized only to a very small extent with β-phenylethyl acetate and not at all with β-phenylethyl benzoate or mesitoate.



$$\overbrace{CH_2CO}^{-}{-}O{-}CH_2{-}\overset{H}{C}HC_6H_5 \xrightarrow{^-NH_2}$$

$$C_6H_5CH{=}CH_2 + (CH_2CO_2)^{=} \xrightarrow{NH_3} CH_3COO^-$$

With excess potassium amide, α-phenylethyl acetate (or α-phenylisobutyl acetate) appears to be converted to its anion but, in contrast to β-phenylethyl acetate, β-elimination does not occur and the ester is regenerated on acidification. However, similar to β-phenylethyl acetate, α-phenylethyl acetate undergoes the acetoacetic ester reaction in the presence of less than an equivalent of potassium amide.

It has been found that with alcoholic potassium hydroxide (which cannot ionize appreciably the α-hydrogen), α,β-diphenylethyl acetate readily undergoes hydrolysis at room temperature to form the corresponding alcohol; no stilbene was found.[9] Similarly, β-phenylethyl acetate has been reported to undergo hydrolysis with potassium hydroxide.[10]

Experimental[11]

Reactions with Potassium Amide. General Procedure.—In a 500-cc. transparent Dewar flask, equipped with a mercury-sealed stirrer, dropping funnel and drying tube of drierite, was placed liquid ammonia which had been distilled from sodium. The calculated amount of clean potassium was added and its conversion (assumed quantitative) to potassium amide was catalyzed by a piece of rusty iron gauze.

Except in the reactions using excess ester (in which the mode of addition was reversed), a cold solution of the ester in dry ether was added to the stirred liquid ammonia solution of potassium amide. A vigorous reaction generally occurred. The excess potassium amide was destroyed by the addition of solid ammonium chloride (equivalent to the base used) and ice water added carefully. The isolation of the products varied.

β-Phenylethyl Mesitoate with Potassium Amide.—The ester (b. p. 190–192.5° at 4 mm.) was prepared in 75% yield from 0.109 mole each of mesitoyl chloride[12] and β-phenylethyl alcohol in 40 cc. of dry benzene. After standing overnight and refluxing three hours, the cooled reaction mixture was washed with dilute alkali, dried and distilled.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 79.89; H, 7.30.

β-Phenylethyl mesitoate (10.7 g., 0.04 mole) in 30 cc. of ether, with 0.05 mole of potassium amide in 200 cc. of ammonia produced a red solution. The addition required one minute and, after thirty seconds more,[13] ammonium

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(6) See Hauser and Hudson, "Organic Reactions," Roger Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1942, chapter IX.

(7) An intramolecular mechanism in which the negative end of the ester anion removes the β-hydrogen to form directly the acetate ion and styrene apparently does not operate, since excess amide ion is required to produce styrene.

(8) Judging from the relative rates of alkaline hydrolysis of the corresponding ethyl esters, the carbonyl carbon should be only one-tenth as reactive in the benzoate as in the acetate. See Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 212.

(9) Limpricht and Schwanest [*Ann.*, **155**, 65 (1870)] reported that with warm alcoholic potassium hydroxide, α,β-diphenylethyl acetate forms stilbene. Klages [*Ber.*, **35**, 2263, 2264 (1902)] reported that with pyridine α-*p*-methoxyphenylpropyl acetate forms anethole, while Radziszewski [*Ber.*, **7**, 141 (1874)] reported that with potassium hydroxide, α-phenylethyl acetate forms styrene and polystyrene. No yields were given. The olefins might have resulted from pyrolysis.

(10) Radziszewski, *Ber.*, **9**, 373 (1876).

(11) Melting and boiling points are uncorrected. Microanalyses are by Dr. T. S. Ma, University of Chicago, Chicago, Ill.

(12) Fuson, Corse and McKeever, THIS JOURNAL, **61**, 2010 (1939); see also Fuson, Bottorff and Speck, *ibid.*, **64**, 1450 (1942).

(13) Bergstrom and Fernelius [*Chem. Rev.*, **12**, 87 (1933)] state that styrene reacts with potassium amide. In the present work, when β-phenylethyl acetate was allowed to react with a large excess of potassium amide for ten minutes, only a glassy material (presumably polymerized styrene) could be isolated. However, when styrene was allowed to stand with potassium amide in liquid ammonia for one minute, the styrene was recovered essentially unchanged.

chloride, water and ether were added and the mixture shaken. From the aqueous phase was isolated a trace of mesitoamide (m. p. 184–186°; reported, 187–188°).[14] The ether phase, after washing with 15% phosphoric acid, saturated sodium bicarbonate solution and water, was dried with drierite. To the stirred ether solution, chilled in an ice-bath, was added slowly a 5% solution of bromine in carbon tetrachloride until the deep orange color remained for two minutes. The excess bromine was destroyed with saturated sodium bisulfite, the solution dried and the solvent distilled, yielding 5 g. (48%) of styrene dibromide, m. p. 68–70°. After recrystallization from 80% ethanol, the m. p. and mixed m. p. with authentic dibromide was 72–73°.[15]

The sodium bicarbonate extract was acidified with hydrochloric acid, precipitating mesitoic acid. After washing with a little cold water the m. p. and mixed m. p. of the acid was 152–153[16]; yield, 5.6 g. (85%).

β-Phenylethyl Acetate, (A) with Slight Excess of Potassium Amide.—β-Phenylethyl acetate (0.05 mole) in 30 cc. of ether, with 0.055 mole of potassium amide for the same time as in (B) produced no detectable amount of styrene. The original ester (44%) was recovered.

(B) With Large Excess of Potassium Amide.—β-Phenylethyl acetate (0.05 mole) in 25 cc. of ether, with 0.11 mole of potassium amide in 200 cc. of ammonia produced a pink mixture. The addition required one minute and after one minute more the reaction mixture was worked up as described for the mesitoate. The phosphoric acid extraction produced an emulsion which separated only slowly. That portion of the ether phase which had separated within ten minutes was washed, dried and brominated, yielding 4 g. (30%) of styrene dibromide,[17] m. p. 69–71°; after recrystallization, m. p. and mixed m. p., 73–74°. No other product was found. Considerable of the styrene probably remained in the emulsion which was discarded. From the original aqueous ammonium chloride solution there was isolated a trace of β-phenylethylamine; m. p. of benzoyl derivative, 114–115° (reported 116°).[18]

(C) With Excess Ester.—A solution of 0.20 mole of potassium amide in 200 cc. of liquid ammonia was siphoned (using pressure from a nitrogen tank) during two minutes into the stirred solution of 36.1 g. (0.22 mole) of β-phenylethyl acetate in 25 cc. of dry ether. After a few seconds ammonium chloride, water and ether were added and the mixture shaken until all the solid dissolved. The ether phase was washed, dried and the solvent distilled. The residue was fractionated through a 12-cm. Vigreux column, yielding 15.2 g. of material, b. p. 108–115° at 14 mm., and 8.1 g. (39%) of β-phenylethyl acetoacetate b. p. 151.5–153.0° at 6 mm. The mid-fraction of the β-keto ester was analyzed.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.01; H, 6.69.

The β-keto ester gave a red ferric chloride test and a phenylpyrazolone (m. p. 126–127; obtained from equivalents of β-keto ester and phenylhydrazine in glacial acetic acid at 120° for three hours) that was shown by the mixed melting point method to be identical with that obtained from ethyl acetoacetate.[19] The material, b. p. 108–115° at 14 mm., evidently consisted of β-phenylethyl acetate (37%, corresponding to 16% recovery of ester, based on saponification equivalent) and β-phenylethyl alcohol Refluxing the mixture with 20% sodium hydroxide for three hours yielded pure β-phenylethyl alcohol, b. p. 96.0–96.5° at 8 mm.

α,β-Diphenylethyl Acetate with Excess Potassium Amide.—The ester, b. p. 136° at 2 mm., was prepared in 80% yield from α,β-diphenylethyl alcohol and acetic anhydride.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.67. Found: C, 79.9; H, 6.80.

α,β-Diphenylethyl acetate (3 g., 0.0125 mole) in 25 cc. of ether, with 0.11 mole of potassium amide in 100 cc. of ammonia produced a yellow mixture and deposited crystals. After two minutes, ammonium chloride and water were added and the mixture allowed to stand until most of the ammonia had evaporated. Sufficient water was added to dissolve the ammonium chloride and the crystals filtered off and washed with water. Recrystallization from hot 95% alcohol yielded 1.3 g. (58%) of stilbene (large plates), m. p. 124–125.[20] An additional 0.5 g. (22%) of stilbene, m. p. 123–125°, was obtained from the alcoholic filtrate.

β-Phenylethyl Benzoate with Potassium Amide.—Preliminary experiments showed that no styrene is formed. The reaction of 22.6 g. (0.1 mole) of β-phenylethyl benzoate (b. p. 177–178° at 8 mm.) with 0.25 mole of potassium amide in 200 cc. of ammonia produced a white precipitate. After ten minutes ammonium chloride, water and ether were added and, after shaking, the precipitate of benzamide was filtered off. The aqueous and ether phases of the filtrate were separated. Evaporation of the aqueous phase under the hood at room temperature gave more benzamide, the total yield of which (after recrystallization from hot water) was 6.3 g. (51%); the m. p. and mixed m. p. was 125.5–127.0°. The ether phase yielded 7.8 g. (64%) of β-phenylethyl alcohol, b. p. 103–104° at 12 mm.; m. p. of α-naphthylurethan, 117–118°.[21]

α-Phenylethyl Acetate, (A) with Excess Potassium Amide.—The reaction of 0.10 mole of the ester with 0.2 mole of potassium amide in 200 cc. of liquid ammonia was stopped after fifteen minutes, 50% of the original ester being recovered. Apparently no styrene was formed under these conditions nor after a longer or shorter reaction time. Neither was olefin obtained from α-phenylisobutyl acetate under similar conditions.

(B) With Excess Ester.—A solution of 0.2 mole of potassium amide in 200 cc. of liquid ammonia was siphoned into a stirred ether solution of 0.22 mole of α-phenylethyl acetate as described for the corresponding experiment with β-phenylethyl acetate. After fifteen minutes, the mixture was worked up, yielding α-phenylethyl acetoacetate (55%), b. p. 149–151° at 10 mm., giving a red enol test.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.16; H, 6.60.

α,β-Diphenylethyl Acetate with Alcoholic Potassium Hydroxide.—To 50 cc. of 0.4 molar solution of potassium hydroxide in 95% alcohol (purified by distillation from potassium hydroxide), was added at room temperature 2.07 g. (0.0086 mole) of the α,β-diphenylethyl acetate. Titration of aliquots of the resulting solution indicated a very rapid reaction. After twenty-four hours, an equal volume of water was added to the solution, precipitating fine white needles (1.2 g., 70%) of α,β-diphenylethyl alcohol, melting at 65°.[22] More of this solid alcohol was readily obtained from the filtrate. Since stilbene is only slightly soluble even in 95% ethyl alcohol, it is probable that no appreciable amount of it was present.

Summary

1. Bases may react with carboxylic esters not only at the carbonyl carbon or α-hydrogen in the acyl portion but also at the α-carbon or β-hydrogen in the alkoxy portion.

2. With potassium amide in liquid ammonia,

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[14] Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1936, p. 430.

[15] Huntress and Mulliken, "Identification of Pure Organic Compounds," Order 1, John Wiley & Sons, Inc., New York, N. Y., 1941, p. 525.

[16] Ref. 14, p. 430.

[17] The styrene could not have been formed from β-phenylethyl alcohol (which might have resulted from ammonolysis of the ester) since, with potassium amide under similar conditions, this alcohol gave no styrene.

[18] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 194.

[19] Knorr, *Ann.*, **238**, 147 (1887).

[20] Ref. 15, p. 514.

[21] Ref. 18, p. 186.

[22] Ref. 14, p. 386.

β-phenylethyl benzoate exhibits the carbonyl carbon reaction to form benzamide but β-phenylethyl mesitoate undergoes β-elimination to form styrene and mesitoic acid. With an equivalent of potassium amide, β-phenylethyl acetate and α,β-diphenylethyl acetate are converted to their ester anions which, with excess potassium amide, undergo β-elimination to form styrene and stilbene, respectively. With less than an equivalent of potassium amide, β-phenylethyl acetate undergoes the acetoacetic ester reaction.

3. With potassium amide, α-phenylethyl acetate forms its anion which undergoes the acetoacetic ester reaction but fails to exhibit β-elimination. With alcoholic potassium hydroxide, α,β-diphenylethyl acetate undergoes the carbonyl carbon reaction but not β-elimination.

DURHAM, N. C. RECEIVED SEPTEMBER 5, 1944

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Epoxidation of Unsaturated Fatty Materials with Peracetic Acid in Glacial Acetic Acid Solution

BY THOMAS W. FINDLEY, DANIEL SWERN AND JOHN T. SCANLAN

The oxidation of unsaturated fatty materials with peracetic acid in acetic acid solution has been studied by numerous investigators.[2,3,4,5,6] The oxidation products were usually mixtures of hydroxy-acetoxy compounds, which on saponification gave good yields of glycols. In two instances, however, epoxy compounds were isolated. Smit[4] reported the conversion of linoleic acid to diepoxystearic acid, but the yields were not given. King,[6] in a study of the oxidation of oleic and elaidic acids with hydrogen peroxide in acetic acid (peracetic acid was the oxidizing agent), was unable to obtain the high-melting 9,10-epoxystearic acid, m. p. 59.5°, from oleic acid and obtained only 25–30% yields of the low-melting 9,10-epoxystearic acid, m. p. 55.5°, from elaidic acid. However, by using peracetic acid in an inert solvent, such as chloroform or ether, other investigators[7a,b] have obtained good yields of epoxy compounds from cyclohexene and other cyclic olefins. It may be assumed, therefore, that peracetic acid functions as an oxidizing agent in exactly the same way as perbenzoic acid to yield epoxy compounds, but that in acetic acid solution the epoxy ring is opened and mixtures of hydroxy-acetoxy compounds are obtained. This would appear to be a serious drawback to the preparation of epoxy compounds from olefins by peracetic acid oxidation, since peracetic acid is most conveniently prepared and used in acetic acid.

In studying the rate of ring opening of the high-melting 9,10-epoxystearic acid by acetic acid, we have found that at 25° ring opening occurs to the extent of about 1% per hour, whereas at 65 to 100°, the ring is opened quantitatively in one to four hours. King[6] has demonstrated that the high-melting 9,10-epoxystearic acid, when dissolved in acetic acid for one week at room temperature, was almost completely converted to hydroxy-acetoxystearic acids, whereas under somewhat similar conditions, the low-melting 9,10-epoxystearic acid, from elaidic acid, was much more stable, only about 50% being converted to hydroxy-acetoxystearic acids. It is not surprising, therefore, that epoxy compounds were usually not isolated by previous workers who investigated peracetic acid oxidations of olefins in acetic acid solution, since in most cases the reactions were conducted for long periods of time or at elevated temperatures. Either of these conditions would cause the ring to open.

By following the course of the oxidative reaction of peracetic acid with a wide variety of unsaturated fatty materials in glacial acetic acid, it was observed that the reaction was usually complete within two to four hours at room temperature when 1.1–1.2 moles of peracetic acid per mole of double bond were used, 85–95% of the theoretical quantity of peracetic acid being consumed. Upon dilution of the reaction mixtures with water, the products were readily isolated in good yield by filtration or by separation of the oil obtained. The products consisted mainly of epoxy compounds and contained small amounts of unreacted double bond and hydroxy-acetoxy compounds. This reaction is quite general and, when properly controlled, affords a simple and convenient method for the preparation of large quantities of epoxy compounds. It is not necessary to use the peracetic acid in an inert solvent.

The epoxidation reaction was successfully applied to oleic acid, elaidic acid, methyl oleate, methyl 10,11-hendecenoate (methyl undecylenate), methyl ricinoleate, oleyl alcohol, glyceryl trioleate, lard oil, neatsfoot oil, castor oil, olive oil, peanut oil, rapeseed oil, cottonseed oil, corn oil,

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] Boëseken and Belinfante, *Rec. trav. chim.*, **45**, 914 (1926); Boëseken, Smit and Gaster, *Proc. Acad. Sci. Amsterdam*, **32**, 377 (1929).

[3] Hilditch, *J. Chem. Soc.*, **1828** (1926); Hilditch and Lea, *ibid.*, 1576 (1928).

[4] Smit, *Rec. trav. chim.*, **49**, 675, 686, 691 (**1930**).

[5] Scanlan and Swern, THIS JOURNAL, **62,** 2305, 2309 (1940).

[6] King, *J. Chem. Soc.*, 37 (1943).

[7] (a) Arbusow and Michailow, *J. prakt. Chem.*, **127**, 1, 92 (1930), (b) Boëseken and Schneider, *ibid.*, **131**, 285 (1931).