2.00 g. (0.015 mole) of terephthalaldehyde and 2.33 g. (0.015 mole) of benzene-1,4-diacetonitrile in 250 ml. of ethanol held at 5° under an atmosphere of nitrogen. When approximately 10 ml. of the catalyst solution had been added the reaction mixture became yellow in color and an orange-yellow solid began to precipitate. Stirring was continued for approximately 16 hr. at 5° then the orange, solid product was filtered, washed with ethanol and ether, and dried in a vacuum oven. Infrared analysis of a Nujol mull indicated the absence of saturated —C—C—CN and hydroxyl groups and the presence of 5–10% aldehyde groups.

Anal. Found: C, 79.32; H, 4.02; N, 10.28.

Two fusion polymerizations were run on this monomer system using sodium methoxide as the catalyst and no solvent. In both experiments, the equimolar monomer mixture was first heated in a sealed glass ampoule under nitrogen. The ampoule was then opened and heating was continued at atmospheric pressure under a stream of nitrogen.

Polyterephthalylidene. The self-condensation of *p*-tolualdehyde was attempted by both solution and mass polymerizations as above. Sodium ethoxide, pyridine, and piperidine were used as catalysts and absolute ethanol as the solvent in the solution runs.

Thermal decomposition measurements. Thermal decomposition measurements were made on polymers C and D and on Teflon for comparison. A tubular electric furnace and a chainomatic balance were incorporated into an apparatus constructed for thermal gravimetric analysis. The polymers were pyrolyzed under a nitrogen atmosphere.

Acknowledgment. The authors wish to express their appreciation to R. A. Nyquist for assistance in obtaining and interpreting the infrared spectra of the polymers.

MIDLAND, MICH.

[COMMUNICATION NO. 2045 FROM THE RESEARCH LABORATORIES, EASTMAN KODAK CO.]

Bisesteramides of Terephthalic Acid

J. L. R. WILLIAMS, T. M. LAAKSO, K. R. DUNHAM, D. G. BORDEN,
J. VANDENBERGHE, J. A. VANALLAN, AND D. D. REYNOLDS

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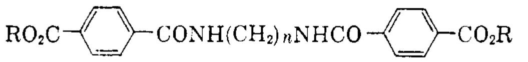
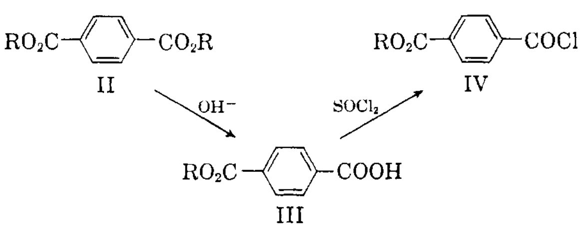
A general synthesis for a new class of bisesteramides I has been devised. Terephthalic esters were hydrolyzed to the ester acids and converted to the acid chlorides which, when treated with the diamine and base, yielded the bisesteramides. Alternate syntheses for specific esteramides are also discussed.

During the investigation of a new class of polyesters, it became necessary to prepare a series of esteramides of the type I.


I

The terephthalic esters (II) were hydrolyzed to the ester acid (III), which, in turn, was converted to the acid chloride (IV) with thionyl chloride.[1] Reaction of two moles of IV with one mole of an aliphatic diamine (V) in the presence of a base gave the required esteramide, I.



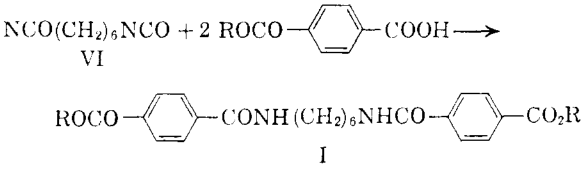
$$2IV + \underset{V}{H_2N(CH_2)_nNH_2} \longrightarrow I$$

The physical constants and analytical data for the bis(4-carboalkoxybenzoyl)alkylenediamines which have been prepared by this method are collected in Table I. Three derivatives of secondary amines are appended at the end of the table.

The required dialkyl terephthalates (II) were prepared by ester interchange from dimethyl terephthalate and the appropriate alcohol using titanium tetrabutoxide as a catalyst.

Formation of the esteramide, I, from IV and V was carried out, using either pyridine or aqueous sodium hydroxide as the acid-acceptor. The latter method was preferred since the use of pyridine led to the formation of colored by-products.

An alternate synthesis of the six carbon esteramides I ($n = 6$) was accomplished by the following isocyanate method:



Where R, = C_2H_5, a yield of 71% was obtained.

During the preparation of *N,N'*-bis(*p*-carbomethoxybenzoyl)hexamethylenediamine, I ($n = 6$; R = CH_3), a high-melting impurity was isolated. Its formation was favored by long reaction times, high temperatures, and excess isocyanate. The high-melting by-product was more evident during a reaction time of fourteen minutes at 225° than at 175° for an hour and a half. Table II summarizes the reaction conditions and yields of various run in a number of solvents.

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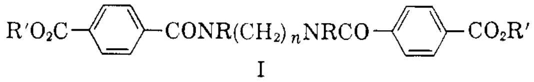
[1] J. B. Cohen and H. S. DePennington, *J. Chem. Soc.*, **113**, 57 (1918).

TABLE I

N,N′-Bis(4-carboalkoxybenzoyl)alkylenediamines


$R'O_2C-C_6H_4-CONR(CH_2)_nNRCO-C_6H_4-CO_2R'$

I

n	R	R′	Compound	Yield, %	M.P., °C.	Empirical Formulas	Analyses Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
0	H	*i*-C_4H_9	*N,N′*-Bis(*p*-carboisobutoxybenzoyl)hydrazine	88.2	180–181	$C_{24}H_{28}N_2O_6$	65.5	6.4	6.4	65.1	6.4	6.4
2	H	CH_3	*N,N′*-Bis(*p*-carbomethoxybenzoyl)ethylenediamine	69	247–248	$C_{22}H_{24}N_2O_6$	64.2	5.8	6.8	64.5	6.1	7.3
2	H	C_2H_5	*N,N′*-Bis(*p*-carbethoxybenzoyl)-ethylenediamine	69	247–249	$C_{22}H_{24}N_2O_6$	64.2	5.8	6.8	64.2	6.1	7.3
2	H	*n*-C_4H_9	*N,N′*-Bis(*p*-carbobutoxybenzoyl)-ethylenediamine	92.6	211–212	$C_{26}H_{30}N_2O_6$	66.7	6.9	6.0	67.1	7.1	5.8
2	H	*i*-C_4H_9	*N,N′*-Bis(*p*-carboisobutoxybenzoyl)ethylenediamine	96.5	194–195	$C_{26}H_{30}N_2O_6$	66.7	6.9	6.0	67.1	6.8	5.8
3	H	*i*-C_4H_9	*N,N′*-Bis(*p*-carboisobutoxybenzoyl)trimethylenediamine	85.6	176–177	$C_{27}H_{34}N_2O_6$	67.2	7.0	7.8	67.4	7.2	7.9
4	H	CH_3	*N,N′*-Bis(*p*-carbomethoxybenzoyl)tetramethylenediamine	75.7	255–256	$C_{22}H_{26}N_2O_6$	64.3	5.8	6.8	64.1	6.1	7.2
5	H	*i*-C_4H_9	*N,N′*-Bis(*p*-carboisobutoxybenzoyl)pentamethylenediamine	86.5	140–141	$C_{29}H_{38}N_2O_6$	68.3	7.4	5.5	68.4	7.3	5.6
6	H	CH_3	*N,N′*-Bis(*p*-carbomethoxybenzoyl)hexamethylenediamine	63.0	232–233	$C_{24}H_{28}N_2O_6$	65.4	6.4	6.4	65.8	6.1	6.2
6	H	C_2H_5	*N,N′*-Bis(*p*-carbethoxybenzoyl)-hexamethylenediamine	88.8	207–208	$C_{26}H_{22}N_2O_6$	66.7	6.8	5.9	67.0	7.1	5.9
6	H	*n*-C_4H_9	*N,N′*-Bis(*p*-carbobutoxybenzoyl)-hexamethylenediamine	94	188–189	$C_{30}H_{40}N_2O_6$	68.7	7.6	5.4	68.8	7.8	5.3
6	H	*i*-C_4H_9	*N,N′*-Bis(*p*-carboisobutoxybenzoyl)hexamethylenediamine	80	165–166	$C_{30}H_{40}N_2O_6$	68.7	7.6	5.4	69.0	7.9	5.3
	CH_3	*i*-C_4H_9	*N,N′*-Dimethyl-*N,N′*-bis(*p*-carboisobutoxybenzoyl)ethylenediamine	51	138–139	$C_{28}H_{31}N_2O_6$	67.7	7.2	5.6	67.3	6.8	5.3
	CH_3	*i*-C_4H_9	*N,N′*-Dimethyl-*N,N′*-bis(*p*-carboisobutoxybenzoyl)hexamethylenediamine	71	81–82	$C_{32}H_{49}N_2O_6$	69.5	7.8	5.1	69.6	8.1	5.4
		CH_3	*N,N′*-Bis(*p*-carbomethoxybenzoyl)piperazine	56.1	230–231	$C_{22}H_{22}N_2O_6$	64.5	5.3	6.8	64.9	4.9	7.1

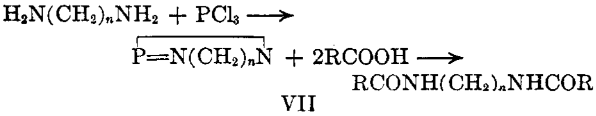
TABLE II

Bisisocyanate Preparation of *N,N′*-Bis(*p*-carbomethoxybenzoyl)hexamethylenediamine

Run	Temperature, °C.	Time, min.	Solvent	Yield, %
1	215	20	None	56
2	215	60	None	53
3	215	90	None	33
4	215	150	None	40
5	175	90	None	50
6	175	45	Dimethylformamide	12
7	175	60	Chlorobenzene	35
8	175	60	*m*-Dichlorobenzene	62–65
9	175	60	*n*-Octane	<2
10	175	60	Dow ethylbenzenes	65
11	175	135	Dioxane	3
12	175	60	Dimethylaniline	44

Although Dow diethylbenzene mixture was shown to be the preferred reaction medium, the reaction temperature remained critical. The diisocyanate method is more satisfactory for the preparation of *N,N′*-bis(*p*-carbethoxybenzoyl)-hexamethylenediamine [I (n = 6; R = C_2H_5)] and *N,N′*-bis(*p*-carbobutoxybenzoyl)hexamethylenediamine [I (n – 6; R = *n*-C_4H_9)] than for the higher-melting *N,N′*-bis(*p*-carbomethoxybenzoyl)-hexamethylenediamine [I (n = 6; R = CH_3)], since the latter must be prepared at temperatures in excess of 200°, a region where secondary reactions occur. Attempts to prepare *N,N′*-bis(*p*-carboisobutoxybenzoyl)hexamethylenediamine [I (n = 6; R = *i*-C_4H_9)] from the diisocyanate failed to produce the desired product.

Two other methods for making the amides [I (n = 6; R = *i*-C_4H_9 and n = 6; R = C_2H_5)] directly from the acid were investigated. The first method consisted in the reaction of phosphorus trichloride with a diamine form a reactive phosphazo derivative (VII) which readily condensed with acids to give amides. This reaction proceeded smoothly, and I (n = 6; R = *i*-C_4H_9) and I (n = 6; R = C_2H_5) have been prepared in yields of 80 to 85%.


$$H_2N(CH_2)_nNH_2 + PCl_3 \longrightarrow$$
$$\overline{P{=}N(CH_2)_nN} + 2RCOOH \longrightarrow RCONH(CH_2)_nNHCOR$$

VII

The second method consisted in preparing the mixed anhydride (IX) from 4-carboisobutoxybenzoic acid and ethyl chlorocarbonate. This mixed anhydride, when treated with hexamethylenediamine, gave a 65 to 70% yield of I ($n = 6$; $R = i\text{-}C_4H_9$).

Preliminary synthetic experiments were carried out in the methyl and ethyl series, the intermediates of which were readily handled in small laboratory-sized runs. In order to take advantage of more favorable solubility characteristics and the resulting ease of handling of larger-scale preparations, the n-butyl and i-butyl systems were used in later preparations.

EXPERIMENTAL

p-Carbomethoxybenzoic acid [III ($R = CH_3$)]. To a solution of 100 g. (0.52 mole) of dimethyl terephthalate [II ($R = CH_3$)] in 150 ml. of refluxing methanol was added a solution of 32.6 g. (0.58 mole) of potassium hydroxide in 600 ml. of water. The saponification was completed in about 10 min. as evidenced by the fact that a sample of the reaction mixture was completely soluble in water. After the addition of an equal volume of water, the diluted reaction mixture was acidified with hydrochloric acid. The white precipitate was collected by filtration. The dried filter cake weighed 61.5 g. (65.5%). Pure III ($R = CH_3$), m.p. 228–230°, was obtained by crystallization from water.

The following acid esters were prepared in a similar fashion using the appropriate alcohol as the reaction medium: p-carbethoxybenzoic acid (III. $R = C_2H_5$), m.p. 169–171° from toluene, 74% yield; p-carboxoisobutoxybenzoic acid (III. $R = i\text{-}C_4H_9$), m.p. 153° from toluene, 69% yield; p-carbobutoxybenzoic acid (III, $R = n\text{-}C_4H_9$), m.p. 132.5–133.5° from toluene, 66% yield.

p-Carbomethoxybenzoyl chloride (IV. $R = CH_3$). A solution of 28.0 g. (0.16 mole) of III ($R = CH_3$) in 32.4 g. (0.3 mole) of thionyl chloride was heated under reflux for 18 hr. Distillation of the reaction mixture gave 27.6 g. (89%) of IV ($R = CH_3$), b.p. 135–138°/10 mm., m.p. 54–55°. p-Carbethoxybenzoyl chloride (IV. $R = C_2H_5$), m.p. 27°, b.p. 133–134°/6 mm.; p-carboisobutoxybenzoyl chloride (IV. $R = i\text{-}C_4H_9$), b.p. 155–157°/7 mm., m.p. 38.5° and p-carbobutoxybenzoyl chloride (IV. $R = n\text{-}C_4H_9$), b.p. 115–118°/0.5 mm., m.p. 13.5°, n_D^{25} 1.5260 were prepared in a similar fashion.

Diisobutyl terephthalate (II. $R = i\text{-}C_4H_9$). In a round bottomed, three-necked, 22-l. flask equipped with a 100-cm. long by 2.5-cm. wide helices-packed column and a partial-takeoff head there was placed 4 kg. (20.6 moles) of dimethyl terephthalate, 14 l. of isobutanol, and 25 ml. of titanium butoxide. By balancing the heat input to the mantle with the takeoff rate, the temperature of the distillate was maintained at 64–68°. After 1500 ml. of distillate was collected, the mantle heat was increased until the temperature reached 105°, at which time distillation was continued for 0.5 hr. The reaction mixture was cooled to 50°. The residual crude ester (II. $R = i\text{-}C_4H_9$) was used directly for the preparation of III ($R = i\text{-}C_4H_9$). Dibutyl terephthalate (II. $R = C_4H_9$) was prepared in a similar fashion. Diethyl terephthalate was prepared according to the method of Koelsch.[2]

N,N'-Bis(p-carbobutoxybenzoyl)ethylenediamine [I ($n = 2$, $R = C_4H_9$)]. a. *Alkali method.* In a 4-l. beaker equipped with an efficient stirrer was placed 19 g. (0.3 mole) of 95% ethylenediamine, 700 ml. of water, and 700 ml. of benzene. To the well stirred mixture was added, dropwise, one half of Solution A [144 g. (0.6 mole) of p-carbobutoxybenzoyl chloride in 150 ml. of benzene]. After 10 min., one half of Solution B [24 g. (0.6 mole) of sodium hydroxide in 150 ml. of water] was added dropwise, followed by one half of the remainder of Solution A and then one half of the remainder of Solution B. The sequence was continued until the addition of both solutions was completed. The viscous slurry was filtered and the solids washed by slurrying with 3-l. portions of hot water. The product, after it had been collected and dried, weighed 133 g. Crystallization from 1800 ml. of butyl alcohol yielded 130 g., 92.6% of I ($n = 2$, $R = C_4H_9$), m.p. 211°.

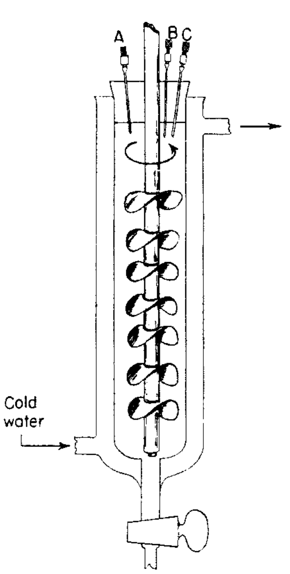


Fig. 1. Continuous Schotten-Baumann reactor

N,N'-Bis(p-carbethoxybenzoyl)hexamethylenediamine [I ($n = 6$, $R = C_2H_5$)]. b. *Pyridine method.* To a solution of 34.8 g. (0.3 mole) of hexamethylenediamine in 500 ml. of pyridine was added dropwise, with stirring, 127.5 g. (0.6 mole) of p-carbethoxybenzoyl chloride. After the addition was complete, the reaction mixture was stirred for 15 min. and poured into an ice-water slurry. The crude product which was collected by filtration was crystallized from 4 l. of ethanol to give 125 g. (88.8%) of I ($n = 6$, $R = C_2H_5$), m.p. 207–208°.

N,N'-Bis(p-carboisobutoxybenzoyl)hexamethylenediamine [I ($n = 6$, $R = i\text{-}C_4H_9$)]. c. *Using a continuous reactor.* In order to prepare larger quantities of this derivative, the glass water-jacketed reactor shown in Fig. 1 was used. The inner section of the reactor was 1.5 in. wide by 24 in. long, the upper end of which was closed with a rubber stopper. Nozzles A, B, and C, the stirrer shaft, and a thermometer were inserted through the stopper. The water jacket served to maintain the reaction temperature at the desired level. Agitation was provided for mixing by the motor-driven shaft bearing three-bladed propellers spaced 0.5 in. apart along its total length. A benzene solution of IV ($R = i\text{-}C_4H_9$) was injected through nozzle B while an aqueous solution of hexamethylenediamine and sodium hydroxide was admitted through nozzle C. Water was added through nozzle A at such a rate that the volume within the reactor remained constant. The reaction was immediate, and the solid product which settled slowly to the bottom of the vessel was withdrawn through the large-bore stopcock. Reaction solutions as follows were prepared: 4329 g. (18 moles) of IV ($R = i\text{-}C_4H_9$) was dissolved in benzene to a total volume of 4860 ml.; 1044 g. (9 moles) of hexamethylenediamine and 760 g. (18 moles) of sodium hydroxide in water to a total volume of 9720 ml. In a typical run, the reactants were added as follows: water, 15 l. per hr.; amine-alkali solution, 7.8 l. per hr.; acid chloride–benzene, 3.9 l. per hr. The agitator was rotated at 100 r.p.m. in such a manner that settling of the solids was

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[2] C. F. Koelsch, *Org. Syntheses*, **26**, 96 (1946).

retarded. By operation of the above procedure at 30° for 1.5 hr., there was obtained after recrystallization from isobutanol, 3850 g. (87%) of I ($n = 6$, R = i-C_4H_9), m.p. 165–166°.

d. *Mixed anhydride method.* *p*-Carboisobutoxybenzoic acid, 22.2 g. (0.1 mole), was dissolved in 100 ml. of dry chloroform and the solution cooled to 0°. Triethylamine, 10.1 g. (0.1 mole), was then added, followed by 10.8 g. (0.1 mole) of ethyl chlorocarbonate. The mixture was maintained at 0–5° for 2 hr., at which time a solution of 5.3 g. (0.05 mole) of hexamethylenediamine in 30 ml. of dry chloroform was added. The temperature of the mixture rose rapidly to 30° and carbon dioxide was evolved. The reaction mixture was allowed to stand at 5° for 18 hr. at which time the chloroform solution was washed with water and dilute sodium carbonate. The chloroform solution was dried over potassium carbonate and distilled to give a residue, which, after crystallization from ethanol, gave 20 g. of I ($n = 6$, R = i-C_4H_9), m.p. 165–166°.

N,N'-Bis(p-carbethoxybenzoyl)hexamethylenediamine [I ($n = 6$; R = C_2H_5)]. e. *Phosphorus trichloride method.* Phosphorus trichloride (3.25 ml.) was added slowly to 4.3 g. of hexamethylenediamine in 20 ml. of pyridine held at 10°. After the reaction mixture was stirred for 0.5 hr. at 20°, a solution of 9.3 g. of *p*-carbethoxybenzoic acid in 25 ml. of warm pyridine was added. The reaction mixture was heated on the steam bath for 3 hr. after which time excess pyridine was distilled at reduced pressure. The residue was stirred sequentially with water, dilute sodium carbonate, and methanol to give 9.4 g. (82%) of I ($n = 6$, R = C_2H_5), m.p. 228–229°.

ROCHESTER, N. Y.

[CONTRIBUTION FROM MELLON INSTITUTE]

Ozonolysis of Fluoranthene[1]

R. H. CALLIGHAN, M. F. TARKER, JR., AND M. H. WILT

Received November 2, 1959

During ozonolysis, a molecule of fluoranthene is attacked by two molecules of ozone. Using aqueous sodium bicarbonate to decompose the active-oxygen-containing products thus formed, fluorenone-1-aldehyde was obtained in high yield along with lesser amounts of fluorenone-1-carboxylic acid. Fluorenone-1-carboxylic acid was obtained in high yield by peracetic acid oxidation of fluorenone-1-aldehyde. A near quantitative yield of the dimethyl acetal of fluorenone-1-aldehyde was obtained by refluxing the aldehyde in methanol in the presence of a trace of peracetic acid. Alkaline cleavage of the dimethyl acetal of fluorenone-1-aldehyde produced the previously unreported isodiphenaldehydic acid in excellent yield. Good yields of isodiphenic acid were obtained by ozone oxidation of the aldehyde-acid. Baeyer-Villiger oxidation of fluorenone-1-carboxylic acid produced the previously unreported 1-carboxy-9-oxa-9,10-dihydrophenanthrene-10-one. The *n*-butyl ester of this lactone was also prepared and characterized.

Fluoranthene (I) reportedly has been ozonized to a mixture of fluorenone-1-aldehyde (II) and fluorenone-1-carboxylic acid (III),[2–4] but the yield was only about 30%. In recent years, there have been many new developments concerning the reaction of ozone with organic compounds.[5] It seemed advisable, therefore, to re-evaluate the action of ozone on fluoranthene in the light of new reactions and techniques. By analogy with the ozonolysis of naphthalene,[6] one might expect that one mole of fluoranthene would react readily with two moles of ozone to give the difficultly accessible 1-substituted fluorenones in high yield. This was indeed found to be so. It should be mentioned that a recent publication by Copeland and co-workers[7] (which appeared after the completion of our work) agrees with our conclusions although the experimental approach was different. Copeland reports an 84% yield of II and an 80% yield of III from the ozonolysis of fluoranthene in an unspecified solvent.

When a suspension of fluoranthene in anhydrous *t*-butyl alcohol was treated with two molecular equivalents of ozone at room temperature, an orange-yellow solution resulted. Titration of the active oxygen showed that 93% of the theoretical was present in the solution. Furthermore, the active oxygen was present as hydroperoxide since a positive test was obtained using lead tetraacetate.[8] It was not hydrogen peroxide, however, because a negative test was obtained with a titanium salt. The distinguishing test is based on the yellow-orange color which is developed by titanic acid in the presence of hydrogen peroxide but which is not developed with other hydroperoxides.[9] Decomposition of the active-oxygen-containing solution by steam distillation resulted in an orange-yellow solid, which was a mixture of fluorenone-1-aldehyde (about 60%) and fluorenone-1-carboxylic acid (about 40%). In addition, the aqueous phase was found to contain glyoxal, hydrogen peroxide, and

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(1) Paper presented before the Division of Organic Chemistry, American Chemical Society, 136th Meeting, Atlantic City, N. J., Sept. 17, 1959.

(2) *The Ozonolysis of Aromatic Compounds: A Literature Survey*, Report No. 0181, The Coal Tar Research Association, April 12, 1957.

(3) H. Vollman, *Ann.*, **531**, 65 (1937).

(4) I. G. Farbenindustrie A. G., British Patent **472,167**, Sept. 14, 1937.

(5) Philip S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(6) P. S. Bailey and F. J. Garcia-Sharp, *J. Org. Chem.*, **22**, 1008 (1957).

(7) P. G. Copeland, R. E. Dean, and D. McNeil, *Chem. & Ind. (London)*, p. 329 (March 7, 1959).

(8) R. Criegee, *Fortschr. chem. Forsch.*, **1**, 536 (1950).

(9) Walter C. Schumb, Charles N. Satterfield, and Ralph L. Wentworth, A.C.S. Monograph No. 128, *Hydrogen Peroxide*, Reinhold Publishing Corporation, New York, 1955, p. 549.