g. (68%) respectively. A solution of 10.2 g. (0.05 mole) of 1-phenyl-3,4-dihydronaphthalene in 60 ml. of carbon tetrachloride at 0° was brominated with 8 g. (2.75 ml., 0.05 mole) of bromine in 100 ml. of carbon tetrachloride to give 8 g. (56%) of the same bromide.

A 3-g. (0.01 mole) sample of this compound was treated with 20 ml. of 0.5*N* sodium hydroxide solution, heated on a steam bath, and a solution of 7 g. (0.04 mole) of potassium permanganate in 60 ml. of water was added over a period of 30 min. After the addition was complete, the solution was heated for an additional 24 hr., and 5 ml. of ethyl alcohol was added to destroy any unchanged permanganate. The solution was acidified with 10 ml. of concd. hydrochloric acid and 1 ml. of 6*N* nitric acid. This mixture was then heated for an additional 2 hr. and allowed to cool to room temperature. The product was extracted with ether and washed with sodium hydroxide solution. The sodium hydroxide solution was acidified with concentrated hydrochloric acid and the product was extracted from the water solution with ether. Evaporation of the ether gave 0.9 g. (36%) of a compound, which after drying for 2 days at reduced pressure over phosphorus pentoxide, melted at 122–125°. A mixed melting point with an authentic sample of *o*-benzoyl benzoic acid was not depressed.

The preparation of 3- or 4-bromo-3,4-dihydronaphthalene was attempted by adding 10.7 g. (0.06 mole) of *N*-bromosuccinimide to a solution of 10.7 g. (0.05 mole) of 1-phenyl-3,4-dihydronaphthalene in 100 ml. of dry carbon tetrachloride. The flask was exposed to an ultraviolet lamp, heated to reflux temperature, and a small amount of benzoyl peroxide added to initiate the reaction. After a short induction period, the reaction proceeded violently with the liberation of bromine and hydrogen bromide. The reaction was complete in 6 hr. and the succinimide was removed by filtration. The solvent was removed and the product distilled at reduced pressure to yield a lower boiling fraction (b.p. 175–182°/1 mm.), which had a deep blue color characteristic of azulene. The higher boiling fraction (b.p. 185–195°/1 mm.), was redistilled to afford 2 g. of product containing bromine (b.p. 192°/1 mm.).

Anal. Calcd. for $C_{16}H_{13}Br$: C, 67.37; H, 4.59. Found: C, 69.04; H, 4.04.

A sample of this bromo compound was treated with alcoholic potassium hydroxide to yield 1-phenylnaphthalene. The 4-bromo and 4-nitro derivatives of 1-phenylnaphthalene melted at 68–69° and 128–130°, respectively (lit.[22] m.p. 70° and 132°). The same derivatives were obtained from the low boiling fraction of the reaction product.

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(22) R. Weiss and K. Woidich, *Monatsh. Chem.*, **46**, 456 (1925).

[CONTRIBUTION FROM MELLON INSTITUTE]

The Ozonolysis of Acenaphthylene[1]

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The ozonolysis of acenaphthylene was studied in the participating solvents, methanol and *t*-butyl alcohol. In the case of methanol, the first isolable product was 3-hydroxy-7-methoxy-4,5,6-(1,8-naphtho)-1,2-dioxacycloheptane, which was apparently formed by cyclization of the 8-formyl-1-naphthylmethoxymethyl hydroperoxide previously reported by Criegee. With *t*-butyl alcohol, presumptive evidence for the presence of an analogous uncyclized hydroperoxide was obtained. This hydroperoxide apparently did not cyclize.

The conversion of these primary ozonolysis products to 1,8-naphthalenedialdehyde, 1,8-naphthalic acid, 1,8-naphthaldehydic acid, methyl 8-formyl-1-naphthoate, and 1,8-naphthalide in fair to good yields was also part of this study. The dialdehyde was isolated as the bis(*p*-nitrophenylhydrazone) in 39% yield. Infrared examination of the aldehyde-acid and its methyl ester showed that these compounds exist in lactonic forms rather than as uncyclized compounds.

In his review article on *Organic Peroxides*, Criegee indicated that acenaphthylene (I) on ozonolysis in methanol yielded 8-formyl-1-naphthylmethoxymethyl hydroperoxide (II).[2] Details of this experiment have not been published, but recent studies by Bailey[3] on the ozonolysis of phenanthrene in methanol and by Warnel and Shriner[4] on the ozonolysis of indene in ethanol have demonstrated the presence of analogous hydroperoxides or the cyclic peroxides (hemiperacetals) formed by cyclization of intermediate formyl-alkoxymethyl hydroperoxides.

In the present study, acenaphthylene in methanol at -30° was treated with 1.06 molecular equivalents of ozone. A white crystalline solid was isolated by quickly filtering the cold reaction mixture and washing the solid with cold petroleum ether. The solid melted at 115–116° dec. but gradually decomposed at room temperature.

Assignment of the structure 3-hydroxy-7-methoxy-4,5,6-(1,8-naphtho)-1,2-dioxacycloheptane (III) to this compound was based on (a) a correct elementary analysis, (b) satisfactory analyses for active oxygen and methoxyl, (c) a negative hydroperoxide test,[5] and (d) the absence of a carbonyl band and the presence of a hydroxyl band in the infrared spectrum of the compound.

Structure III is obviously the hemiperacetal formed by cyclization of II as anticipated from the observation of Bailey that alkoxy hydroperoxides

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

(2) R. Criegee, *Fortschr. chem. Forsch.*, **1**, 508 (1950).

(3) P. S. Bailey, *J. Org. Chem.*, **23**, 1089 (1958). *J Am. Chem. Soc.*, **78**, 3811 (1956).

(4) J. L. Warnel and R. L. Shriner, *J. Am. Chem. Soc.*, **79**, 3165 (1957).

(5) R. Criegee *et al.*, *Chem. Ber.*, **72**, 1799 (1939).

obtained from the ozonolysis of cyclic molecules appear not to exist in the simple hydroperoxide form if the other end of the chain contains an aldehyde group.[6]

The best yield of hemiperacetal which could be obtained was about 25%. Ozonolysis in a carbon tetrachloride-methanol mixture (3 to 1 by volume) did not increase the yield even though the hemiperacetal is insoluble in carbon tetrachloride. The use of excess ozone (more than one molecular equivalent) lowered the yield, probably because of some attack of ozone on the naphthalene nucleus. No ozone escaped unabsorbed when an excess was used, and the parent compound, acenaphthene, absorbed at least two moles of ozone.

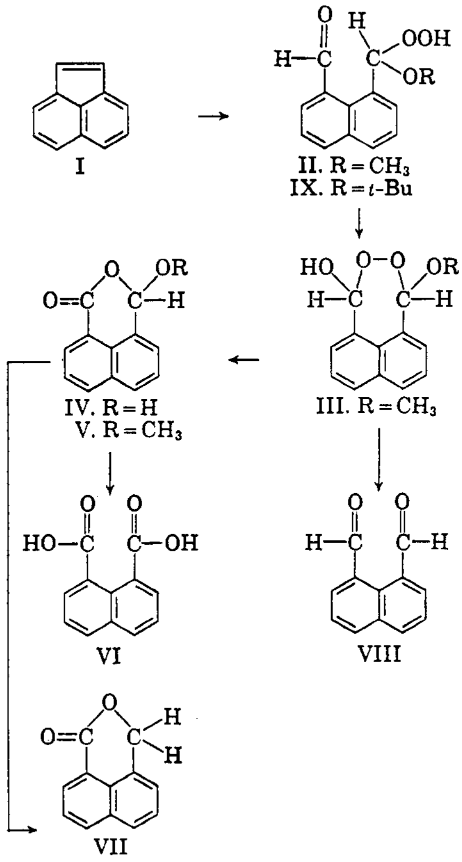
After removal of the hemiperacetal, the methanol solution contained 1,8-naphthaldehydic acid (IV) and methyl 8-formyl-1-naphthoate (V). A 5–10% yield of IV was isolated by evaporating the solvent, treating the residual oil with sodium bicarbonate solution, extracting neutral material with chloroform, and then acidifying the bicarbonate solution. The neutral oily material extracted with chloroform was identified as V on the basis of its infrared spectrum. Neither the aldehyde-acid (IV) nor the aldehyde-ester (V) gave a derivative with 2,4-dinitrophenylhydrazine at room temperature, indicating that both compounds probably exist as the cyclic lactones rather than as the uncyclized derivatives. The infrared spectra of both compounds are in agreement with this conclusion.

It was shown that the material recovered from the methanol filtrate after removal of the hemiperacetal could be oxidized with alkaline hydrogen peroxide to give 1,8-naphthalic acid[7] (VI) in 50% yield. In a publication which appeared after the completion of the present study, Copeland and coworkers reported that acenaphthylene on absorption of one mole of ozone gave an 88% yield of naphthalic anhydride.[8]

When the reaction mixture from the ozonolysis of acenaphthylene in cold methanol was decomposed with sodium hydroxide, the aldehyde-acid (IV) was obtained in about 50% yield, probably because of saponification of the aldehyde-ester V. The neutral product in this case was the lactone, 1,8-naphthalide[9] (VII), which was probably formed by an intermolecular Cannizzaro reaction of the aldehyde-acid IV. A good yield (65.4%) of 1,8-naphthaldehydic acid (IV) was also obtained by ozonizing acenaphthylene in methanol containing a trace of pyridine. On working up the reaction mixture, a 15% yield of 1,8-naphthalide (VII) was obtained as a neutral fraction.

Methyl 8-formyl-1-naphthoate (V) was obtained as a crystalline product in 50% yield by refluxing the hemiperacetal (III) in methanol. The material was identical with an authentic sample prepared by the method of Zink.[10] Reduction of the hemiperacetal with potassium iodide yielded 1,8-naphthalenedialdehyde[11] (VIII) in 38% yield. The compound was isolated as the bis(p-nitrophenylhydrazone).

1,8-Naphthalide (VII) was obtained as a major product by evaporating the methanol after a typical ozonization and treating the residue with formaldehyde and potassium hydroxide. After acidification and washing with bicarbonate solution, crude naphthalide was obtained in 77.6% yield.



In an effort to isolate an uncyclized hydroperoxide of the type reported by Criegee, the ozonolysis of acenaphthylene in t-butyl alcohol was studied. It was thought that the anticipated t-butoxymethyl hydroperoxide might cyclize with difficulty because of the bulky t-butoxy group.

The solution obtained by treating acenaphthylene in t-butyl alcohol at 30° with 1.1 molecular equivalents of ozone was found to contain 92% of the anticipated active oxygen. The solution gave a positive test for hydroperoxide with lead tetraacetate and a negative test for hydrogen peroxide

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(6) P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957).

(7) C. Graebe, *Chem. Ber.*, **26**, 2354 (1893).

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

(9) R. C. Fuson and G. Munn, *J. Am. Chem. Soc.*, **71**, 1870 (1949).

(10) J. Zink, *Monatsh.*, **22**, 986 (1901).

(11) R. Criegee, L. Kraft, and B. Rank, *Ann.*, **507**, 194 (1933).

with titanium^{III} chloride. A positive test with 2,4-dinitrophenylhydrazine indicated the presence of a carbonyl group. These tests were interpreted as indicating the presence of an uncyclized *t*-butoxymethyl hydroperoxide (IX) in the *t*-butyl alcohol solution.

Attempts to isolate IX were only partially successful. A portion of the solution from an ozonolysis in *t*-butyl alcohol was lyophilized at −30° to remove the solvent. The resulting unstable, white sticky solid had an infrared spectrum showing a broad hydroxyl band at 2.8–3.0 μ and a carbonyl band at 5.8 μ. An alkoxy determination gave only about half the theoretical *t*-butoxy content.

On steam distilling the *t*-butyl alcohol solution, a distillate containing a trace of hydrogen peroxide was obtained. The principal solid isolated from the residue was 1,8-naphthaldehydic acid (IV) (some polymeric ozonide was also present in the solid), indicating that most of the anticipated hydrogen peroxide was apparently consumed in oxidizing the 1,8-naphthalenedialdehyde which would result from the hydrolysis of the hydroperoxide.

A sample of acenaphthylene polymeric ozonide prepared in chloroform was decomposed in *t*-butyl alcohol containing aqueous sodium bicarbonate. Along with some undecomposed ozonide, 1,8-naphthaldehydic acid was obtained as the major product.

The results obtained in *t*-butyl alcohol are in agreement with Bailey's comments on the mechanism of ozonization proposed by Milas.[12] The evidence for the formation of a *t*-butoxymethyl hydroperoxide on ozonolysis of acenaphthylene in *t*-butyl alcohol seems best explained as an addition of the alcohol to a Criegee-type zwitterion rather than the decyclization of a hemiperacetal.

EXPERIMENTAL

The acenaphthylene used in this work was commercial material, m.p. 90°, and was estimated to be of 98 to 99.5% purity. The methanol and *t*-butyl alcohol were reagent-grade materials.

A Welsbach Corporation Model T-23 laboratory ozonator was used in this work. Commercial oxygen was dried to a dew point of at least −60° F. with a laboratory "Lectrodryer" sold by the Pittsburgh Lectrodryer Corporation.

The reaction vessel most often used was a 500-ml. gas-washing bottle with the gas inlet at the bottom, a 6-cm. fritted disk sealed in just above the inlet to disperse the incoming gases, and the outlet at the top. The reaction vessel was equipped with a magnetic stirrer and a reflux condenser to return solvent from the gas stream. Ozone concentrations were determined with a Welsbach Model C ozone meter or iodometrically as detailed in the "Welsbach Basic Manual of Applications and Laboratory Ozonization Techniques."

3-Hydroxy-7-methoxy-4,5,6-(1,8-naphtho)-1,2-dioxacycloheptane (III). A solution of purified acenaphthylene (10 g., 0.066 mole) in methanol (200 ml.) was treated with approximately 2.3 weight per cent ozone (in oxygen) at a flow rate of 102 l. per hr. at a temperature of −30° (Dry Ice-alcohol bath) for 65 min. Under these conditions, a 1.06 molecular equivalent (3.36 g., 0.07 mole) of ozone was passed into the reaction mixture. After flushing with dry oxygen, the cold reaction mixture was filtered to remove the precipitated hemiperacetal, washed with petroleum ether (b.p. 60–68°), and dried in a vacuum desiccator. When dry, the white powdery hemiperacetal weighed 4.0 g. (26.2% yield) and melted at 115–116° dec.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.2; H, 5.2; active oxygen, 6.90; OCH_3, 13.35. Found: C, 67.47; H, 5.51; active oxygen, 6.34; OCH_3, 13.17.

The compound gave a negative hydroperoxide test with lead tetraacetate.[5] The infrared spectrum showed an OH band at 3.0 μ and an ether band at 9.2 μ.

1,8-Naphthaldehydic acid (IV). Ten grams of acenaphthylene in 200 ml. of methanol containing 2 ml. of pyridine was treated with 3.6 g. of ozone at 30° as described previously. The almost colorless solution was poured into a 1-l. flask which contained 200 ml. of 7% aqueous sodium bicarbonate solution. The methanol was then removed by distillation. The insoluble neutral material which remained was removed by filtration yielding 1.8 g. (15% yield) of crude 1,8-naphthalide which melted at 135–148°. The aqueous bicarbonate solution was acidified with concentrated hydrochloric acid yielding 8.6 g. (65.4% yield) of crude 1,8-naphthaldehydic acid which melted at 146–154° dec. Recrystallization from aqueous ethanol raised the melting point to 167–168°. Pure 1,8-naphthaldehydic acid is reported to melt at 167–168°.[9]

The infrared spectrum showed an "alcoholic" OH band at 3.0 μ, a lactone carbonyl band at 5.9 μ, and a C—O—C band at 9.3 μ.

Methyl 8-formyl-1-naphthoate (V). A solution of 3-hydroxy-7-methoxy-4,5,6-naphtho-1,2-dioxacycloheptane (1.7 g., 0.0074 mole) in 50 ml. of methanol was allowed to reflux for 4 hr. The solution was then concentrated to a volume of about 25 ml. on the steam bath, and 25 ml. of water was added. Crystallization occurred, and the product was removed by filtration and dried yielding 0.8 g. (50% yield) of crude methyl 8-formyl-1-naphthoate which melted at 93–96°. After recrystallization from aqueous ethanol, the compound melted at 102–104°, and a mixed melting point with an authentic sample showed no depression. The authentic sample was prepared starting with 1,8-naphthaldehydic acid according to the method of Zink[10] and melted at 102–104° after recrystallization. Zink reported a melting point of 105°.

Anal. Calcd. for $C_{13}H_{10}O_3$: C, 72.9; H, 4.67; OCH_3, 14.48; saponification number, 214. Found: C, 72.57; H, 4.61; OCH_3, 14.13; saponification number, 219.

The infrared spectrum showed a lactone carbonyl band at 5.8 μ and a C—O—C band at 9.2 μ.

1,8-Naphthalic acid (VI). Acenaphthylene (20 g.) was ozonized in methanol according to the procedure described previously. The insoluble hemiperacetal was removed by filtration, and the filtrate was made alkaline by adding 100 ml. of 5% sodium hydroxide. This alkaline mixture was then allowed to reflux for about 1 hr. to form the sodium salt of 1,8-naphthaldehydic acid. The solution was neutralized to *p*H 7 with hydrochloric acid, and 34 ml. of 50% hydrogen peroxide was added. The solution was then allowed to reflux for an additional 30 min. After cooling, the solution was acidified with concentrated hydrochloric acid yielding 14.7 g. (51.8% yield) of crude 1,8-naphthalic acid which melted at 229–267° dec. and had a neutralization equivalent of 115. Recrystallization from aqueous ethanol raised the melting point to 268–269° dec. Pure 1,8-naphthalic acid melts at 270° dec. and has a neutralization equivalent of 108.[7]

1,8-Naphthalide (VII). Acenaphthylene (10 g.) dissolved in 200 ml. of methanol was treated with 3.4 g. of ozone at 30° as described previously. After flushing with dry oxygen, water (150 ml.) was added and the methanol removed by distillation. An oil separated from the remaining aqueous fraction. The mixture was cooled in an ice water bath and

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(12) N. A. Milas, P. Davis, and J. T. Nolan, Jr., *J. Am. Chem. Soc.*, **77**, 2536 (1955).

solid potassium hydroxide (50 g.) added over a 30-min. period so that the temperature did not rise above 70°. Formaldehyde (15 ml. of 40% solution) was added and the temperature maintained between 75° and 85° for 3.5 hr., an additional 10 ml. of formaldehyde being added at the end of the first hour. The reaction mixture was acidified, and the white solid which formed was collected on a filter and washed with sodium bicarbonate solution, yielding 9.4 g. (77.6% yield) of crude 1,8-naphthalide melting at 129–148°. Recrystallization (charcoal treatment) from an ethyl acetate–petroleum ether (b.p. 60–71°) mixture yielded 5.7 g. (47% yield) melting at 155–157°. This is the same melting point reported by Fuson and Munn.[9]

The infrared spectrum showed a lactone carbonyl band at 5.8 μ and a C—O—C band at 9.2 μ.

1,8-Naphthalenedialdehyde (VIII). A slurry of III (5.0 g.) with 50 ml. of methanol was treated with 10 g. of potassium iodide and 10 ml. of glacial acetic acid. An exothermic reaction liberating iodine occurred. After 1 hr., the iodine was reduced with 10% sodium thiosulfate solution and the solvent evaporated in an air blast. An oil (4.1 g.) separated, which did not crystallize on standing overnight. The oil gave a positive test with 2,4-dinitrophenylhydrazine, and its infrared spectrum showed the presence of OH and carbonyl groups. Criegee[11] reports that the dialdehyde exists as a monohydrate, which would explain the presence of the OH band. One gram of the oil was allowed to react with 2.6 g. of *p*-nitrophenylhydrazine in ethanol containing a few drops of glacial acetic acid. Filtration yielded 0.9 g. (39% yield) of the bis(*p*-nitrophenylhydrazone) as red needles which melted at 227° dec. Criegee reports a melting point of 229° for this derivative.[11]

Anal. Calcd. for $C_{24}H_{18}N_6O_4$: C, 63.40; H, 3.97; N, 18.53. Found: C, 62.90; H, 4.15; N, 18.40.

Ozonolysis in t-butyl alcohol. Ten grams of acenaphthylene dissolved in 100 ml. of *t*-butyl alcohol was treated with 3.6 g. of ozone as described previously. After flushing with dry oxygen, a portion of the solution was frozen in a Dry Ice–acetone bath and the *t*-butyl alcohol removed by lyophilization for 5 hr. at 0.1 mm. while maintaining the sample at −30°. A sample of the white sticky solid was analyzed immediately for *t*-butoxy content.

Anal. Calcd. for $C_{16}H_{18}O_4$: *t*-butoxy, 26.0. Found: 13.6.

The infrared spectrum of the unstable solid showed a broad OH band at 2.8–3.0 μ and a carbonyl band at 5.8 μ.

Titration of an aliquot of the *t*-butyl alcohol solution showed 60 mmoles of active oxygen, which is 92% of the theoretical value of 66. The solution gave a positive carbonyl test with 2,4-dinitrophenylhydrazine reagent, a positive hydroperoxide test with lead tetraacetate, and a negative test for hydrogen peroxide with titanium^{III} chloride.

The remainder of the *t*-butyl alcohol solution was steam-distilled to remove the alcohol, yielding 11.3 g. of a yellow oil which solidified. By extraction with benzene, 6.4 g. of 1,8-naphthaldehydic acid IV melting at 161–165° was obtained.

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PITTSBURGH 13, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WYOMING]

Formation of Phenols in the Reductive Ozonolysis of Aryl Allyl Ethers. Product Analysis with Gas-Liquid Chromatography[1]

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The reductive ozonolysis of a series of *para*-substituted aryl allyl ethers has been found to proceed essentially normally to give more than 75% yield of the corresponding 2-phenoxyethanol. The small amount of phenolic product, estimated from gas chromatograms, is largely due to alkaline cleavage of the ether bond during the reduction procedure. Similar experiments with crotyl phenyl ether have resulted in no significant quantity of phenolic product. These results stand in contrast with some abnormal ozonolyses of allylic compounds in the literature.

Abnormal or unexpected products from the ozonolysis of allylic compounds in nonhydroxylic solvents have been noted by a number of investigators.[3] In the studies with a variety of allylic structures Young[4] and his collaborators reported, in addition to the expected acetic acid, 15% of formic acid obtained in the ozonization and subsequent oxidation of crotyl phenyl ether. A similar treatment of crotyl *p*-nitrophenyl ether yielded 8% of formic acid. The formation of this product, found in the analysis for volatile acids, has been explained in terms of the hydrolytic cleavage of an abnormal or rearranged ozonide resulting from the influence of unshared electron pairs on an electro-negative atom joined to the allylic system. Comparable results[5] were obtained in our laboratories in experiments with oxidative ozonolysis of other aryl allyl ethers which yielded an unexpected phenolic substance. The products isolated from the ozonization-oxidation treatment of allyl (I) and γ-ethylallyl (II) ethers of methyl *o*-cresotinate were *o*-cresotinic acid (IV) as well as the expected 2-carboxy-6-methylphenoxyacetic acid (III). Since a test of the effect of the acidic and alkaline conditions accompanying the oxidation and hydrolysis steps showed that they were responsible for no

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[1] Much of the work reported here was presented at the Ozone Symposium, Division of Organic Chemistry, American Chemical Society, September 1959, Atlantic City, N. J.

[2] Research Corporation Fellow, 1957–58.

[3] P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

[4] W. G. Young, A. C. McKinnis, I. D. Webb, and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 293 (1946).

[5] S. J. Rhoads, R. Raulins, and R. D. Reynolds, *J. Am. Chem. Soc.*, **76**, 3456 (1954).