In the cases where propylene oxide or cyclohexene oxide were used in this procedure, they were added at a controlled rate dropwise at the top of the tube and the reaction was continued until addition was complete.

In the cases where tentatively identified dithiolane or thiophene derivatives were present, the crude reaction product was partitioned through vapor phase chromatography and various portions were analyzed by mass spectrophotometer and infrared spectroscopy. Since authentic samples of the materials were not available the identification is, at the present time, tentative.

*Acknowledgments.* The authors gratefully acknowledge the mass spectrometric analyses performed by Mr. H. R. Harless and the infrared absorption studies conducted by Dr. H. F. White and Mr. C. M. Lovell. They also wish to thank Dr. Harry Wasserman of Yale University for his helpful advice in the preparation of this paper

SOUTH CHARLESTON, W. VA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE AMERICAN UNIVERSITY OF BEIRUT]

# Unsaturated Bile Acid Derivatives. II. Desulfurizations with Raney Nickel[1]

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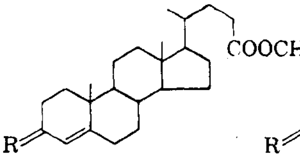
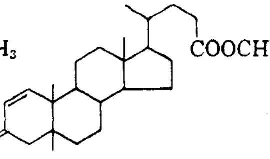
The preparation of methyl $\Delta^4$-cholenate, methyl 3-keto-$\Delta^1$-cholenate, and a compound tentatively regarded as methyl $\Delta^1$-cholenate is described.

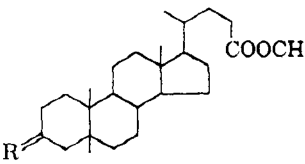
In a previous paper[4] we reported the preparation of methyl 3-keto-$\Delta^4$-cholenate and the epimeric 3-hydroxy-$\Delta^4$-cholenic acids from hyodesoxycholic acid. Extending our work on unsaturated bile acids we would now like to report the preparation of methyl $\Delta^4$-cholenate (Ic), methyl 3-keto-$\Delta^1$-cholenate (IIa) and a compound to which we are assigning tentatively the structure methyl $\Delta^1$-cholenate (IIc).



Ia. R = O
b. R = $\begin{array}{l}CH_2{-}S\diagdown\\ |\\ CH_2{-}S\diagup\end{array}$
c. R = $H_2$



IIa. R = O
b. R = $\begin{array}{l}CH_2{-}S\diagdown\\ |\\ CH_2{-}S\diagup\end{array}$
c. R = $H_2$



IIIa. R = O
b. R = $H_2$

For the preparation of methyl $\Delta^4$-cholenate (Ic), methyl 3-keto-$\Delta^4$-cholenate[4,5] was used as our starting material. Initial attempts to convert Ia to Ib by addition of boron fluoride etherate to an acetic acid solution of the ketone and excess ethanedithiol or by addition of boron fluoride etherate to a solution of the ketone in ethanedithiol[6] led to the formation of oils which solidified only upon prolonged cooling and were difficult to purify. However, crystalline ethylenethioketal (Ib) could be prepared easily and in high yield by treatment of a methanolic solution of the ketone with ethanedithiol and boron fluoride etherate. This procedure gave excellent results also in the preparation of ethylenethioketals from $\Delta^4$-cholestene-3-one and methyl 3-ketocholanate.

The next step in the synthesis was desulfurization with Raney nickel of the ethylenethioketal (Ib) to methyl $\Delta^4$-cholenate. This method, introduced by Hauptmann[7] in the steroid series, has found extensive use in recent years. Desulfurization of unsaturated ethylenethioketals may or may not be accompanied by saturation of the double bond depending on the type of Raney nickel catalyst used and on the position of the double bond in the molecule.[8] In attempting to find out

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(4) M. J. Haddadin and C. H. Issidorides, *J. Org. Chem.*, **25**, 403 (1960).

(5) C. H. Issidorides, M. Fieser, and L. F. Fieser, *J. Am. Chem. Soc.*, **82**, 2002 (1960).

(6) L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

(7) H. Hauptmann, *J. Am. Chem. Soc.*, **69**, 562 (1947).

(8) Some examples reported: (a) $\Delta^4$-cholestene-3-one ethylenethioketal to $\Delta^4$-cholestene, ref. 7; (b) 5-Furosten-3$\beta$-ol acetate 26-ethylenethioketal to 5-furosten-3$\beta$-ol acetate [C. Djerassi, O. Halpern, G. R. Pettit, and G. H. Thomas, *J. Org. Chem.*, **24**, 1 (1959)]; (c) 7,7,10-Trimethyl-$\Delta^{1(9)}$-octal-2-one ethylenethioketal to 7,7,10-trimethyl-$\Delta^{1(9)}$-octalin [F. Sondheimer and S. Wolfe, *Can. J. Chem.*, **37**, 1870 (1959)]; (d) Methyl 12-(ethylenedithio)-3$\alpha$-hydroxy-$\Delta^{9(11)}$-etiocholenate to methyl 3$\alpha$-hydroxy-$\Delta^{9(11)}$-etiocholenate [R. Casanova, C. W. Shoppee, and G. H. R. Summers, *J. Chem. Soc.*, 2983 (1953)]; (e) $\Delta^1$-Cholestene-3-one ethylenethioketal to cholestane [Pl. A. Plattner, A. Fürst, and H. Els, *Helv. Chim. Acta*, **37**, 1399 (1954)]; (f) $\Delta^4$-Cholestene-3,6-dione 3-monoethylenethioketal to cholestane-6-one, ref. 6.

the specific action of W-2 Raney nickel[9] on Ib, three procedures were tried:

*Procedure 1:* The ethylenethioketal in methanol was refluxed with active W-2 catalyst. The product obtained, probably a mixture of methyl cholanate and methyl allocholanate, contained no sulfur and gave a negative tetranitromethane test. The melting point, after chromatography and repeated recrystallizations, was 75–80°; $[\alpha]_D$ +19°; no infrared band at 810 cm.$^{-1}$[10]

*Procedure 2:* The ethylenethioketal in acetone was refluxed with partially deactivated W-2 Raney nickel according to the method of Spero, McIntosh, and Levin.[11] An unsaturated product was obtained (positive tetranitromethane test; broad and undefined band at 795–805 cm.$^{-1}$) which could not be purified easily by recrystallization. Purification *via* the dibromide gave methyl $\Delta^4$-cholenate (Ic) (m.p. 92–93°; $[\alpha]_D$ +71°; sharp band at 810 cm.$^{-1}$).

*Procedure 3:* The ethylenethioketal dissolved in 1:1 acetone-methanol was refluxed with W-2 Raney nickel without prior deactivation. Purification by crystallization gave Ic directly in high yield. Similar results were obtained when the last two procedures were employed for the preparation of $\Delta^4$-cholestene from $\Delta^4$-cholestene-3-one ethylenethioketal. Procedure 2 gave a product inferior to the one obtained by Procedure 3.

From the above findings it appears that selective desulfurizations of unsaturated ethylenethioketals with active W-2 Raney nickel in the presence of acetone may sometimes offer distinct advantages over the well established method of prior deactivation of the catalyst with acetone. It is probable that the carbonyl group of the solvent acts as an *in situ* partial deactivator of the catalyst, hindering the saturation of the double bond.[12]

The molecular rotation difference Ia ($M_D$ 336 chloroform) −Ic ($M_D$ 265 chloroform) is found to be −71, in agreement with the value −72 calculated for the difference in passing from $\Delta^4$-cholestene-3-one ($M_D$ 354 chloroform[13]) to $\Delta^4$-cholestene ($M_D$ 282 chloroform[14]).

For the preparation of methyl $\Delta^1$-cholenate (IIc), methyl 3-keto-$\Delta^1$-cholenate (IIa) was used as our starting material. Compound IIa was prepared recently[5] by manganese dioxide oxidation of methyl 3$\beta$-hydroxy-$\Delta^1$-cholenate, the latter compound being one of several products obtained by selenium dioxide oxidation of a mixture of methyl $\Delta^2$- and $\Delta^3$-cholenate. The successive chromatography, digitonin precipitation, and fractional crystallization steps of this method are lengthy and tedious. During this investigation, the same approach was essentially followed for the preparation of IIa but the procedure was considerably simplified by omitting the digitonin precipitation and fractional crystallization steps. The method we recommend is as follows: The mixture obtained from the selenium dioxide oxidation is acetylated and then subjected to preliminary purification by chromatography. Hydrolysis of the allylic acetates followed by manganese dioxide oxidation of the 3-hydroxy acids (as the methyl esters) gives a mixture of the two isomeric ketones Ia and IIa, separable by chromatography.

Hydrogenation[5] of IIa yielded the corrresponding saturated ketone IIIa, identical with an authentic sample of methyl 3-ketocholanate prepared by Oppenauer oxidation of methyl lithocholate (melting point, mixed melting point, $[\alpha]_D$ and infrared spectrum). Conversion of IIa to IIb was effected with ethanedithiol and boron fluoride etherate in the usual manner.[6]-Previous attempts to condense a similar ketone in the cholestane series with ethanedithiol in the presence of hydrogen chloride, gave a mixture of products.[15] No such difficulty was experienced in the present case. The condensation product IIb had a sharp melting point, unchanged upon repeated recrystallizations. Furthermore, the elemental analysis corresponded to the formula $C_{27}H_{42}O_2S_2$, excluding the formation of undesirable sulfur-rich by-products, a phenomenon previously observed in the case of $\Delta^1$-cholestene-3-one.[15]

Desulfurization of IIb with active W-2 Raney nickel in methanol was accompanied by complete saturation of the double bond. The product isolated was pure methyl cholanate (IIIb), identical (melting point, mixed melting point $[\alpha]_D$ and infrared spectrum) with an authentic sample. Desulfurization with W-2 Raney nickel in acetone-methanol according to Procedure 3, gave an unsaturated product responding to tetranitromethane. In view of the finding of Striebel and Tamm[16] that desulfurization of $\Delta^1$-cholestene-3-one ethylenethioketal with Raney nickel yields $\Delta^2$-cholestene instead of the expected $\Delta^1$-isomer, the possibility that our unsaturated product is methyl $\Delta^2$-cholenate cannot be excluded.

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[9] R. Mozingo, *Org. Syntheses*, Coll. Vol. III, 181 (1955).

[10] P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch, and G. W. Wood, *J. Chem. Soc.*, 2402 (1951).

[11] G. B. Spero, A. V. McIntosh, and R. H. Levin, *J. Am. Chem. Soc.*, 70, 1907 (1948).

[12] In this connection, the remarkable finding of Rosenkranz, Kaufmann, and Romo [J. Am. Chem. Soc., *71*, 3689 (1949)], during their investigation on 3-thioenol ethers of $\Delta^4$-3-keto steroids, is of interest. Desulfurization of the 3-benzylthioenol ether of $\Delta^4$-androstene-3,17-dione with fully active W-2 Raney nickel in dioxane-ethanol gave a mixture of $\Delta^{3,5}$-androstadiene-17-one and androstan-17$\beta$-ol. The interpretation given by the "Syntex" investigators is that the carbonyl group of the thioether molecule at $C_{17}$ acted as a partial deactivator of the nickel hindering the saturation of the double bonds. When the carbonyl group was reduced to the alcohol group, its influence disappeared and the double bonds were saturated.

[13] L. F. Fieser, *Org. Syntheses*, **35**, 43 (1955).

[14] L. F. Fieser and M. Fieser, *Steroids*, Reinhold Publishing Corporation, New York, 1959, p. 253.

[15] Ref. 8 (e).

[16] P. Striebel and Ch. Tamm, *Helv. Chim. Acta*, **37**, 1094 (1954).

However, the molecular rotation difference between our product ($M_D$ 209 chloroform) and methyl cholanate ($M_D$ 79 chloroform) is found to be +130, which is appreciably different from the value −24 reported[17] for the effect on molecular rotation of the introduction of a double bond at position 2 in the 5β series. In view of this, we would tentatively like to assign structure IIc to this product. We are investigating this product further and will report on it at a later date.

## EXPERIMENTAL[18]

*Methyl 3-keto-$\Delta^4$-cholenate ethylenethioketal* (Ib). A solution of methyl 3-keto-$\Delta^4$-cholenate[4] (2 g.) in methanol (30 ml.) was treated with ethanedithiol (1 ml.) and freshly distilled boron fluoride etherate (1 ml.). On cooling, the turbid solution deposited a solid which was collected and washed with cold methanol; yield 2.2 g. (92%), m.p. 107–109°. Repeated recrystallizations from methanol gave feathery needles of Ib melting at 110–111°; $[\alpha]_D$ + 109° (*c* 1.1).

*Anal.* Calcd. for $C_{27}H_{42}O_2S_2$ (462.61): C, 70.07; H, 9.15; S, 13.86. Found: C, 70.05; H, 9.19; S, 13.80.

*Methyl $\Delta^4$-cholenate* (Ic). The ethylenethioketal (Ib) (2 g.) in methanol (50 ml.)-acetone (50 ml.) was refluxed with active W-2 Raney nickel[9] (*ca.* 25 g.) with efficient stirring for 12 hr. The hot reaction mixture was filtered and the clear filtrate was evaporated under reduced pressure. Recrystallization of the residue from methanol gave needles of methyl $\Delta^4$-cholenate (Ic) (1.3 g., 81%) melting at 89–91°. The analytical sample melted at 92–93°; $[\alpha]_D$ +70° (*c* 1.2); positive tetranitromethane test; $\lambda_{cyclohexane}$ 810 cm.$^{-1}$.

*Anal.* Calcd. for $C_{25}H_{40}O_2$ (372.57): C, 80.59; H. 10.82. Found: C, 80.59, H. 10.84.

Another sample of the ethylenthioketal (Ib) in acetone was refluxed for 12 hr. with deactivated W-2 Raney nickel.[11] After the usual work-up, a product was obtained which could not be purified by recrystallizations. The crude product was dissolved in ether and treated with excess bromine in acetic acid. The resulting yellow solution was washed with 5% sodium bicarbonate and water, dried, and evaporated to dryness under reduced pressure. Two recrystallizations of the residue from acetone gave the dibromide melting at 130–132°. The dibromide was shaken at room temperature with excess sodium iodide in acetone (1.5 g./10 ml.), diluted with water and extracted with ether. The ether extracts were treated with a few drops of sodium thiosulfate solution, washed with water, dried, and evaporated to dryness. Recrystallization from methanol gave needles of Ic melting at 92–93°; $[\alpha]_D$ + 71°.

When the Raney nickel desulfurization of Ib was carried out in methanolic solution using active W-2 catalyst, a product was obtained which, after repeated recrystallizations and chromatography, melted at 75–80°; $[\alpha]_D$ + 19° (*c* 1.4); negative tetranitromethane test; no infrared band at 810 cm.$^{-1}$ This product is probably a mixture of methyl cholanate and methyl allocholanate.

*Methyl 3-keto-$\Delta^1$-cholenate* (IIa). A mixture (5 g.) of methyl $\Delta^2$-cholenate and methyl-$\Delta^3$-cholenate (obtained by dehydrotosylation of methyl 3α-tosyloxycholanate[6]) in acetic acid (55 ml.) was treated with selenium dioxide (1.3 g.) dissolved in water (3.7 ml.)–acetic acid (25 ml.). The solution was stirred at room temperature for 35 hr. The resulting red mixture was diluted with ether (200 ml.), washed repeatedly with 5% sodium bicarbonate and water, and filtered from the precipitated selenium. The clear yellow filtrate was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness under reduced pressure. The residue was dissolved in dry pyridine (60 ml.), treated with acetic anhydride (30 ml.), and allowed to stand overnight. The solution was poured with stirring into cracked ice and the solid was removed by filtration, washed with water, dried, dissolved in benzene (5 ml.), and adsorbed on a column of alumina (150 g.). The column was washed slowly with petroleum ether (b.p. 40°–70°) (200 ml.) and then eluted rapidly with petroleum ether–benzene (1:4). The petroleum ether–benzene fraction was evaporated to dryness and the solid residue was refluxed with 2.5*N* methanolic potassium hydroxide (70 ml.) for 1.5 hr. After dilution and acidification of the cooled solution, ether extraction afforded a mixture of hydroxycholenic acids. Esterification with diazomethane in the usual manner gave a mixture of the methyl esters (3 g.).

A solution of the methyl esters (5 g.) in chloroform (500 ml.) was stirred for 3 hr. at room temperature with freshly prepared manganese dioxide,[19] filtered, and evaporated under reduced pressure. The residue was dissolved in benzene (7 ml.) and chromatographed on alumina (100 g.). The column was eluted slowly with ten 80-ml. fractions of petroleum ether (b.p. 40–70°) (Fractions 1–10), then rapidly with fifteen 80-ml. fractions petroleum ether–benzene (4:1) (Fractions 11–25).[20] Fractions 3–10 were combined, evaporated to dryness, dissolved in benzene (2 ml.), and rechromatographed on alumina (30 g.). The column was washed with petroleum ether (150 ml.) and eluted with 500 ml. of petroleum ether–benzene (4:1). The petroleum ether–benzene fraction, upon evaporation and recrystallization from methanol, gave needles of methyl-3-keto-$\Delta^1$-cholenate (IIa) (600 mg.) m.p. 137–138°; $[\alpha]_D$ + 113° (*c* 1.2); $\lambda^{CH_3OH}$ 231.5 mμ. (lit.[5] m.p. 138.5–139.5°; $\lambda^{CH_3OH}$ 231–232 mμ).

*Methyl 3-keto-cholanate* (IIIa) was obtained by hydrogenation of IIa with palladium charcoal in ethanol.[5] The product melted at 117–119°; $[\alpha]_D$ + 31.6° (*c* 1.3). It was identical with an authentic sample obtained by Oppenauer oxidation of methyl lithocholate (melting point, mixed melting point, $[\alpha]_D$ and infrared).

*Methyl 3-keto-$\Delta^1$-cholenate ethylenethioketal* (IIb). Methyl 3-keto-$\Delta^1$-cholenate (IIa) (200 mg.) was treated with ethanedithiol (0.2 ml.) and boron fluoride etherate (0.2 ml.), allowed to stand at room temperature for 20 min., diluted with methanol (20 ml.), and cooled in an ice bath for several hours. The solid was removed by filtration and washed with cold methanol. Recrystallization from methanol gave IIb (200 mg.), melting at 109–110°; $[\alpha]_D$ + 125°.

*Anal.* Calcd. for $C_{27}H_{42}O_2S_2$ (462.61): C, 70.07; H, 9.15; S, 13.86. Found: C, 69.96; H, 9.07; S, 13.49.

*Methyl cholanate* (IIIb). Desulfurization of IIb with active W-2 Raney nickel in methanol gave IIIb, needles from methanol, m.p. 86–87°, $[\alpha]_D$ + 21° (*c* 1.3), identical (melting point, mixed melting point, $[\alpha]_D$, infrared spectrum) with an authentic sample prepared by desulfurization with active W-2 Raney nickel of the ethylenethioketal of methyl 3-ketocholanate.

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(17) Ref. 14, p. 178.

(18) Melting points are uncorrected. Rotations (rounded off to the nearest integer) were measured in chloroform solution. Alumina used for chromatography was neutral grade I "Woelm" to which 3% water was added. Ultraviolet spectra were measured with a Beckman DU quartz spectrophotometer. Infrared spectra were run on a Perkin-Elmer Model 137 Infracord double beam spectrophotometer. Microanalyses by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

(19) F. Sondheimer, O. Mancera, M. Urquiza, and G. Rosenkranz, *J. Am. Chem. Soc.*, **77**, 4145 (1955).

(20) Fractions 11–25, upon evaporation and recrystallizations of the residue from methanol, gave methyl 3-keto-$\Delta^4$-cholenate (Ia) (1.5 g.), m.p. 125–126.5°; $[\alpha]_D$ +87° (*c* 1.25).

*Methyl $\Delta^{1}$-cholenate* (IIc) (*tentative*). Treatment of IIb (100 mg.) with W-2 Raney nickel (*ca.* 8 g.) in acetone (25 ml.)-methanol (25 ml.), as previously described for the preparation of Ic, gave a solid which, upon recrystallization from aqueous methanol, melted at 42–44°. The melting point remained unchanged upon further crystallizations; $[\alpha]_D$ + 56° (*c* 1.2); positive tetranitromethane test.

*Anal.* Calcd. for $C_{25}H_{40}O_2$ (372.57): C, 80.59; H, 10.82. Found: C, 80.34; H, 11.18.

*Acknowledgment.* We are grateful to the Research Corporation and to the Arts and Sciences Research Committee of the American University of Beirut for financial support, and to Professors Kenneth Sauer and Leiper Freeman for many stimulating discussions.

BEIRUT, LEBANON

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, IMPERIAL OIL LTD.]

# Organic Sulfur Compounds. III. Co-Oxidation of Mercaptans with Styrenes and Indene

ALEXIS A. OSWALD[1a]

*Received March 4, 1960*

Co-oxidation of mercaptans and styrenes or indene by air in hydrocarbon solution at 0° results in the formation of substituted 2-mercaptoethyl hydroperoxides. These hydroperoxides are unstable and are readily converted to the corresponding isomeric 2-sulfinylethanols. The reactions reported may be important in causing hydrocarbon fuel instability.

Kharasch and co-workers[1b] were the first to show that mercaptans and olefins co-oxidize in an atmosphere of oxygen at room temperature to yield substituted 2-sulfinylethanols. For the formation of these compounds, Kharasch tentatively suggested a chain mechanism with two reaction routes having a hydroperoxide and an alkoxy radical intermediate.

Ford, Pitkethly, and Young[2] examined the co-oxidation of benzenethiol and indene in greater detail. On the basis of peroxide determination, they have obtained 2-phenylmercapto-1-indanyl hydroperoxide in 77% yield although they did not isolate the product.

In this laboratory, preliminary studies[3] showed that, on aeration of hydrocarbon solutions of aromatic mercaptans and reactive olefins at 0°, the hydroperoxide intermediates of such co-oxidation reactions can be isolated. More detailed studies of the co-oxidation of mercaptans with styrenes and indene, reported here, were made primarily to relate such reactions to the rapid peroxidation of cracked petroleum distillates containing mercaptans and olefins.[4]

*Formation of 2-mercaptoethyl hydroperoxides.* Aeration of hydrocarbon solutions containing an aromatic mercaptan and styrene or α-methylstyrene or indene, each at 0.3 mole/l. concentration at 0°, resulted in a rapid peroxidation. After a few hours' air introduction, almost colorless oils separated. These oils contained a high percentage of hydroperoxide according to both the iodide[5] and the ferrous sulfate[6] methods. A typical member of these new hydroperoxides is 1-(2-naphthylmercapto)-2-phenyl-2-propyl hydroperoxide. This was obtained by the co-oxidation of 2-naphthalenethiol and α-methylstyrene and had a m.p of −10° and a peroxide content of 85%. The co-oxidation product of 2-naphthalenethiol and indene, 2-(2-naphthylmercapto)-1-indanyl hydroperoxide showed exceptional stability; and could be isolated as a colorless solid in a substantially pure state.

*n*-Dodecanethiol did not form any hydroperoxide under similar conditions. For example, with styrene, no reaction was evident even after six hours' aeration at room temperature. However, when the reaction mixture was irradiated by an ultraviolet lamp, 9% yield of solid co-oxidation product with a peroxide content of 13% was obtained after thirty minutes reaction time.

The above results indicate that the co-oxidation of styrenes and indenes with both aromatic and aliphatic thiols results in hydroperoxides. The chain mechanism of the reaction is supported by earlier work on thiol-olefin addition[7–9] and co-oxidation.[1,2]

*Rearrangement to 2-sulfinylethanols.* The aforementioned substituted 2-mercaptoethyl hydroperoxides are usually unstable at room temperature, and rearrange to the more stable corresponding 2-sulfinylethanols. The latter are colorless, crystalline compounds, mostly melting with decomposition (Table I and II). On the basis of this

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(6) C. D. Wagner, R. H. Smith, and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 980 (1947).

(7) T. Posner, *Ber.*, **38**, 646 (1905).

(8) F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928).

(9) A. A. Oswald, *J. Org. Chem.*, **25**, 467 (1960).