tral, dried, and evaporated to dryness. Recrystallization of the residue from aqueous methanol gave 0.45 g., m.p. 209–211°. A second recrystallization from methanol raised the melting point to 211–213°; $[\alpha]^{24}D$ +98.5° (chloroform).

Anal. Calcd. for $C_{25}H_{34}O_6$: C, 64.92; H, 7.41. Found: C, 64.94; H, 7.51.

B.—A solution of 0.10 g. of 21-acetoxypregnan-17α-21-diol-3,11-dione (VII) in 2 ml. of pyridine was treated with 1 equivalent of acetic anhydride (0.45 ml. of a solution of acetic anhydride in pyridine, containing 0.0054 g. of acetic anhydride per ml.). After six hours at room temperature the solution was poured into water and the white crystals which separated were collected with suction, washed and dried: weight 0.09 g., m.p. 210–212°. There was no change in m.p. on crystallization from ether. A mixed melting point with the diacetate obtained in (A) above showed no depression, and the infrared spectra of the two compounds were identical.

Pregnan-17α,21,21-triol-3,11,20-trione (VIII).—A solution of 0.09 g. of crude 21,21-diacetoxypregnan-17α-ol-3,-11,20-trione in 8 ml. of methanol was combined with a solution of 0.20 g. of potassium bicarbonate in 2 ml. of water. A white precipitate which formed immediately was dissolved by gentle warming for five to ten minutes. The solution was allowed to stand at room temperature for five hours, diluted with water and extracted several times with methylene chloride. The combined organic extracts were washed once with water and the wash reëxtracted once with methylene chloride. The solution was dried with magnesium sulfate and evaporated, leaving 0.06 g. of a light tan solid. Crystallization from aqueous isopropyl alcohol gave the hydrated glyoxal VIII, m.p. 169–170.4° (with bubbling), $[\alpha]^{21}D$ +87.0° (ethanol).

Anal. Calcd. for $C_{21}H_{28}O_5 \cdot H_2O$: C, 66.64; H, 7.99. Found: C, 67.50; H, 7.95.

Crystallization from benzene gave the unhydrated form, m.p. 187–188°.

Anal. Calcd. for $C_{21}H_{28}O_5$: C, 69.97; H, 7.83. Found: C, 69.53; H, 8.50.

Solutions of VIII in non-polar solvents such as benzene gave a yellow color characteristic of glyoxals.

Bromination of 21-Acetoxypregnan-17α-ol-3,11,20-trione (II) in *t*-Butyl Alcohol–Methylene Chloride.—A solution of 1.00 g. of 21-acetoxypregnan-17α-ol-3,11,20-trione in 10 ml. of methylene chloride and 10 ml. of *t*-butyl alcohol was combined with a solution of 0.40 g. of bromine in 5 ml. of methylene chloride and 5 ml. of *t*-butyl alcohol. After 1.5 hours at room temperature, the red bromine color had discharged. The methylene chloride was removed by distillation under reduced pressure until crystallization began and the residual solution was poured into 200 ml. of cold water. The precipitate was collected, washed with water and dried at 50°; weight 1.11 g., $[\alpha]^{21}D$ +87.1° (acetone). Recrystallization of 1.00 g. from aqueous acetone gave two crops. The first crop which weighed 0.65 g. was 4-bromo-21-acetoxypregnan-17α-ol-3,11,20-trione (III), $[\alpha]^{26}D$ +100.7° (acetone); while the second crop of 0.17 g. was 21-bromo-21-acetoxypregnan-17α-ol-3,11,20-trione (V), $[\alpha]^{26}D$ +74.5° (acetone).

By treatment of the 21-bromide with sodium iodide in acetic acid as described previously, the starting material (II) was regenerated.

Repetition of the above reaction in darkness, with a trace of benzoyl peroxide, required four hours and a higher percentage of the 4-bromide was formed. Upon recrystallization the first crop weighed 0.75 g., $[\alpha]D$ +104.5° (acetone). The second crop weighed 0.17 g., $[\alpha]^{24}D$ +88.4° (acetone). From this rotation it was apparent that only about half of the second crop consisted of the 21-bromide.

BLOOMFIELD, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

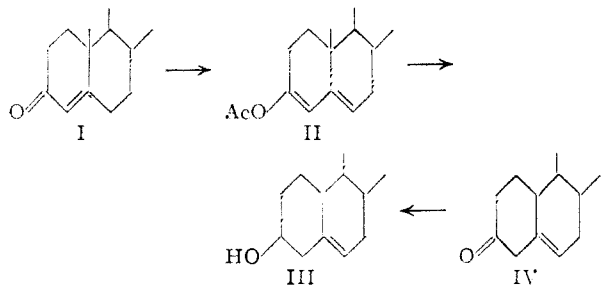
The Reduction of Steroidal Enol Acetates with Lithium Aluminum Hydride and Sodium Borohydride

BY WILLIAM G. DAUBEN, ROBERT A. MICHELI AND JEROME F. EASTHAM

RECEIVED JANUARY 22, 1952

The enol acetates of cholestanone and coprostanone were prepared using isopropenyl acetate and their structures were shown to be Δ^2 and Δ^3, respectively. Each enol acetate was reduced with lithium aluminum hydride and it was found that carbon–carbon double bond reduction occurred. The ratio of α- and β- isomers formed from the enol acetates was different from that obtained by reduction of the parent ketones; a larger amount of the less available isomer was always formed from the enol acetate. The same enol acetates were reduced with sodium borohydride and it was found that the product composition was identical with that obtained by direct reduction of the ketone. The reduction of Δ^4-cholesten-3-one was reinvestigated and it was found that approximately 70% of the β-isomer was formed, a result in contrast to the previously reported equal amounts of the α- and β-compounds.

It has recently been reported that both lithium aluminum hydride[1] and sodium borohydride[2–4] reduce 3-acetoxy-$\Delta^{3,5}$-cholestadiene (Δ^4-cholesten-3-one enol acetate, II) to cholesterol (III). The presence of two double bonds in II makes it atypical as an enol acetate and raises the question of the structural requirements for the above type of reaction. If the reduction could be applied to simple enol acetates, then the reaction might be of utility for a purpose more general than the rather unique task of transforming an α,β-unsaturated ketone into a β,γ-unsaturated alcohol.[5] For example, in the reduction of a steroidal ketone to an alcohol, there exists the possibility that both isomeric alcohols will be formed. It was found in the above enol acetate case, however, that whereas sodium borohydride reduction gave an isomer ratio similar



I II III IV

(1) W. G. Dauben and J. F. Eastham, THIS JOURNAL, 73, 3260 (1951).

(2) E. Schwenk, M. Gut and J. Belisle, *Arch. Biochem. Biophys.*, 31, 456 (1951).

(3) B. Belleau and T. F. Gallagher, THIS JOURNAL, 73, 4458 (1951).

(4) W. G. Dauben and J. F. Eastham, *ibid.*, 73, 4463 (1951).

(5) For an extension of the method to the transformation of an α, β, γ-, δ-unsaturated ketone into a β, γ-, δ, ε-unsaturated alcohol, see W. G. Dauben, J. F. Eastham and R. A. Micheli, *ibid.*, 73, 4496 (1951).

to that obtained by direct reduction of Δ^5-cholesten-3-one (IV),[6] lithium aluminum hydride produced quite a different ratio of products. Since in many preparative procedures one isomer may be more desirable than its epimer, it was thought of interest to investigate the problem further to see if the reaction could be employed to change the ratio of isomers usually obtained by direct reduction of the ketone. The enol acetates of cholestanone and coprostanone have been used for such a study.

The enol acetates, Δ^2-3-acetoxycholestene (VI) and Δ^3-3-acetoxycoprostene (XI), were prepared by allowing cholestan-3-one (V) and coprostan-3-one (X), respectively, to react with isopropenyl acetate. The direction of enolization of these ketones is indicated from previous studies of the bromination[7] and the sulfonation[8] of the parent ketone and the structures VI and XI would be expected. Direct experimental evidence for the position of the double bond was obtained by ozonization of VI to the dicarboxylic acid VII and of XI to the acid XII. In addition, bromination of the enol acetate of cholestanone yielded 2-bromocholestan-3-one. Such results establish the structure of the enol acetate of cholestanone (VI) as a Δ^2-compound and of coprostanone (XI) as a Δ^3-compound.[9] Recently, Inhoffen[10] prepared the enol ethers of these ketones by the pyrolysis of the diethyl acetal and found a similar bond structure for his compounds.

The reduction of the enol acetates, VI and XI, has been performed using lithium aluminum hydride in the normal fashion (ester to hydride) and by the inverse method (hydride to ester). The technique employed was essentially that used in the previous work with cholestenone enol acetate.[1] The products formed from VI, *viz.*, cholestanone (V), cholestanol (VIII) and epicholestanol (IX), could be separated directly by chromatography on alumina. The products from XI, *viz.*, coprostanone (X), coprostanol (XIII) and epicoprostanol (XIV), could only be separated into a stanol and a stanone fraction by chromatography and the individual stanols finally separated by digitonin. The results of these reductions are reported in Table I. For comparison, the data of Shoppee and Summers[6] on the direct reduction of the ketones and the results of the present investigation on inverse reduction of the parent ketones have been included in the same table.

It is interesting to note that there is some effect due to the inverse mixing of the reactants in the reduction of the free ketone and of the enol acetate. The yield of the less available isomer is increased in all cases. It is also notable that the ratio of isomers obtained from the reduction of the enol acetate is quite different from the ratio obtained with the free ketone. Although the use of the enol acetate does not go so far as to reverse the epimer ratio, as might be hoped, approximately three to four times as much of epicholestanol and coprostanol were formed. Another observation to be made from Table I is that some parent ketone is always found in the reduction mixture from enol acetates. It has previously been reported[1] that cholestenone can be isolated from the lithium aluminum hydride reduction of cholestenone enol acetate.[11]

TABLE I

PER CENT. YIELD OF COMPOUNDS FORMED ON REDUCTION

Compound	LiAlH$_4$ Normal α	Normal β	Normal one	Inverse α	Inverse β	Inverse one	NaBH$_4$ α	NaBH$_4$ β
Δ^4-Cholesten-3-one (I)	24	70	..	16	72	..	24	69
Δ^4-Cholesten-3-one enol acetate (II)[a]	15	34	27	16	34	34	13	75[b]
Δ^5-Cholesten-3-one (IV)	5	90[c]	..	..	..	..	23	72
Cholestanone (V)	4	91[c]	..	12	82	..	13	84
Cholestanone enol acetate (VI)	17	58	21	20	59	10	13	84
Coprostanone (X)	94	4[c]	..	87	7	..	76	16
Coprostanone enol acetate (XI)	70	13	10	63	20	8	..	...

[a] See ref. 1. [b] See ref. 4. [c] See ref. 6.

(6) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 687 (1950).

(7) A. Butenandt and A. Wolff, *Ber.*, **68**, 2091 (1935); C. Djerassi and C. Scholz, *Experientia*, **3**, 107 (1947).

(8) A. Windaus and E. Kuhr, *Ann.*, **532**, 52 (1937); **538**, 116 (1938).

(9) In the abstract of Am. Chem. Soc. Meeting (Cleveland, 1951, p. 99M) B. Armbrecht and M. Rubin reported the preparation of these same enol acetates by another method employing acetic anhydride and acetyl chloride. No physical properties were given and it was mentioned that the enol acetate of cholestanone was shown to have the Δ^2-structure by ozonolysis but no absolute determination of the structure of the coprostanone compound was given.

(10) V. H. Inhoffen, G. Stoeck, G. Kolling and U. Stoeck, *Ann.*, **568**, 181 (1950).

(11) A possible mechanism for the reduction of enol acetates by lithium aluminum hydride will be the subject of a future communication.

Shoppee and Summers[6] have discussed the possible reasons for the high degree of stereospecificity in the reduction of steroidal ketones with lithium aluminum hydride. It was noted, however, that whereas Δ^5-cholesten-3-one (IV) and 7-ketocholesteryl acetate produced mainly the β-isomer, Δ^4-cholesten-3-one, a compound of similar planarity as the other unsaturated ketones, has been reported[12] to yield the α- and β-isomers in about equal amounts. Recently, Schmutz, Schaltegger and Sanz[13] have found that the reduction of $\Delta^{4,6}$-cholestadien-3-one gave the β-isomer in 93% yield. In view of the discrepancy in the results of the Δ^4-isomer, its reduction has been reinvestigated. It was found that regardless of the conditions of the reaction, a higher per cent. of the Δ^4-cholesten-3-β-ol (70–72%) was always obtained. This result falls nicely into line with the high degree of stereospecificity of such reductions of α,β-unsaturated ketones.

The four ketones, I, IV, V and X and the two enol acetates, II and VI, have been reduced with sodium borohydride. The results from these reductions are also shown in Table I. The reactions were conducted in aqueous methanol.[14] It can be seen that there is no great difference between the reduction of the free ketone with lithium aluminum hydride and with sodium borohydride. Apparently, the less available isomer is formed to a slightly greater amount when borohydride is used. Of greater significance is a comparison of the results from the reduction of the enol acetates by these two reagents. The ratio of isomers from the enol acetates II and VI with borohydride are similar to the ratios obtained from the parent ketones I and V. This is in marked contrast to the results obtained with the aluminum hydride. In further contrast to the results with this latter reagent, no ketone is recovered from the borohydride reductions. These facts are consistent with the hypothesis that when sodium borohydride is employed, the enol acetate first undergoes solvolysis to the free ketone which in turn is reduced.

Thus it appears that when the technique of reducing an enol acetate is to be employed for the concomitant purpose of transposing a carbon–carbon double bond,[1-4] it is best to use sodium borohydride because of the simplified experimental technique and because of the greater yield of alcohol (no ketone recovered). If the method is to be used in an attempt to change the isomer ratio obtained by reduction of the free ketone then lithium aluminum hydride must be employed.

Experimental[14]

Cholestanone Enol Acetate.—To 4.0 g. (10.3 mmoles) of cholestanone (m.p. 127.5–128.5°) there was added a mixture of 4.5 ml. of isopropenyl acetate and 0.02 ml. of concentrated sulfuric acid. The solution was refluxed for one hour under nitrogen, the pressure slightly reduced and 1.5 ml. of liquid distilled in the course of 30 minutes. To the brown, viscous oil there was added 0.1 g. of anhydrous sodium acetate and a few ml. of chloroform and the resulting mixture warmed. The solution was decanted from the salts into 50 ml. of absolute methanol and upon warming and the addition of more chloroform, if necessary, a clear solution was obtained. Upon slow cooling the product crystallized, yield 3.86 g. (87%), m.p. 87–88°. After two recrystallizations from methanol–chloroform the cholestenol acetate melts from 90.0–90.5° (cor.), $[\alpha]^{25}D$ +56.9° (*c* 2.05).

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.25; H, 11.29; mol. wt., 429. Found: C, 81.12; H, 10.90; sapn. equiv., 437.

Coprostanone Enol Acetate.—Coprostanone (3.0 g., 7.8 mmoles., m.p. 56.5–57.5°) was allowed to react with 4.0 ml. of isopropenyl acetate and a trace of sulfuric acid as described above. After the removal of the solvents, the viscous, brown oily product was dissolved in ether and washed successively with cold 2 *N* hydrochloric acid, 0.5 *N* sodium hydroxide and water. The ethereal solution was dried and the product evaporatively distilled at a bath temperature of 120–130° and 10^{-5} mm. pressure. The pale yellow distillate crystallized upon standing and yielded 3.30 g. (99%) of analytical pure enol acetate, m.p. 77–79°. A small sample was recrystallized from acetone–methanol, m.p. 83.1–83.6° (cor.), $[\alpha]^{25}D$ +37.2° (*c* 1.96).

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.25; H, 11.29; mol. wt., 429. Found: C, 81.32; H, 11.21; sapn. equiv., 414.

Care should be taken to see that the compound is thoroughly dried before storing as it has a tendency to decompose when not entirely free of solvent.

Bromination of Cholestanone Enol Acetate.[15]—A solution of bromine (1.5 mmoles) in 3 ml. of carbon tetrachloride was added slowly to a cold solution of the enol acetate (0.5 g., 1.2 mmoles) in 3 ml. of carbon tetrachloride. After one hour, 6.5 ml. of cold methanol was added and the solution allowed to stand at room temperature for two days. An equal volume of water was then added and the organic phase separated, washed with sodium bicarbonate solution, dried and evaporated. Crystallization of the product from acetone–methanol yielded 2-bromocholestan-3-one, m.p. 170–173° (lit.[7] 169–170°).

Ozonization of Cholestanone Enol Acetate.—A cold (−10°) solution containing 1.0 g. (2.3 mmoles) of the enol acetate in 60 ml. of absolute ethyl acetate and 60 ml. of glacial acetic acid was treated with 5 mmoles of ozone during a period of 15 minutes. Hydrogen peroxide (10 ml. of 3%) was added and the solution allowed to stand at room temperature for 18 hours. The reaction mixture was then evaporated at reduced pressure and the residue refluxed for one hour with 40 ml. of 5% methanolic potassium hydroxide. The solution was diluted with aqueous base and extracted with ether to remove 0.26 g. of oily neutral material. Acidification and further extraction of the aqueous phase yielded 0.75 g. of solid, white, acidic product. Recrystallization of this material from ether–hexane yielded 0.23 g. of pure dibasic acid VII, m.p. 195–196° (lit.[10] m.p. 194–196°).

Ozonization of Coprostanone Enol Acetate.—A solution containing 0.4 g. (0.9 mmole) of the enol acetate and 50 ml. of ethyl acetate–acetic acid mixture was treated with ozone and worked-up in a manner similar to that described above. There was obtained 0.34 g. of acid and the material was recrystallized from ether–hexane as needles, yield 0.081 g., m.p. 248–249° (lit.[10] 245–246°).

Inverse Lithium Aluminum Hydride Reduction of Cholestanone Enol Acetate.—To 500 mg. (1.2 mmoles) of the enol acetate in 10 ml. of anhydrous ether there was added dropwise during a period of 30 minutes a clear solution of 8 mmoles of lithium aluminum hydride in 10 ml. of ether. After the solution had been stirred for an additional four hours in an atmosphere of nitrogen, the reduction complex and excess hydride were decomposed with 25 ml. of cold, 2.5 *N* sulfuric acid. More ether was added to the organic phase and the ethereal solution washed with dilute sulfuric acid, saturated aqueous sodium bicarbonate solution, water and then dried. After evaporation of the solvent, the residue

(12) H. McKennis and G. W. Gaffney, *J. Biol. Chem.*, **175**, 217 (1948); P. A. Plattner, H. Heusser and A. B. Julkarni, *Helv. Chim. Acta*, **32**, 266 (1949).

(13) J. Schmutz, H. Schaltegger and M. Sanz, *ibid.*, **34**, 1111 (1951).

(14) The values given in Table I are average results from two or more runs of each reduction indicated. In the Experimental not all of the reductions are given, but sufficient are described to indicate all variation of technique employed. Unless otherwise specified all melting points are uncorrected. Determinations of optical activity were made in chloroform solution. Microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California.

(15) P. Z. Bedoukian, THIS JOURNAL, **71**, 1840 (1949).

(437 mg.) was dissolved in hexane and chromatographed on alumina.[16] Table II summarizes the results.

TABLE II

Compound eluted	Wt., mg.	M.p., °C.	$[\alpha]^{25}D$
V	44	126–127	+41.3° (*c* 1.9)
VIII	269	141–142.5	+22.7° (*c* 3.7)
IX	92	181–183	+24.0° (*c* 1.3)

Normal Lithium Aluminum Hydride Reduction of Coprostanone Enol Acetate.—A solution of 500 mg. (1.2 mmoles) of the enol acetate in 15 ml. of anhydrous ether was added over a period of 30 minutes to an ethereal solution of lithium aluminum hydride (8 mmoles in 15 ml.). The slightly turbid solution was stirred for an additional four hours at room temperature and then processed as described above. Chromatography yielded coprostanone and a mixed stanol fraction. It was possible to separate some epicoprostanol from this mixture by careful elution of the alumina column, but it was more efficient to elute the total stanol fraction and employ digitonin to separate the epimers. The stanols (381 mg.) were dissolved in 40 ml. of hot 90% ethanol and to this solution there was added 0.4 g. of digitonin dissolved in 40 ml. of hot 90% ethanol. The mixture was cooled overnight at ice temperature and the digitonide filtered, dried and then redissolved in 5 ml. of dry pyridine. The pyridine solution was added to 50 ml. of ether and the resulting suspension filtered through supercel. The filtrate was washed with acid, base and water and then dried and evaporated. Crystallization of the residue from ethanol yielded coprostanol. The filtrate from the digitonide preparation was added to a threefold excess of ether, filtered (supercel) and diluted with a large excess of water. The ethereal layer was separated and processed as for the insoluble fraction. A summary of the results is given in Table III.

TABLE III

Compound isolated	Wt., mg.	M.p., °C.	$[\alpha]^{25}D$
X	43	Oil[a]	.....
XIII	60	96–98	+24° (*c* 1.25)
XIV	315	107–109	+30° (*c* 1.67)

[a] The coprostanone isolated by chromatography of the crude reduction mixture frequently defied crystallization until it was evaporatively distilled.

Sodium Borohydride Reduction of Cholestanone Enol Acetate.—A solution of 0.2 g. (5.3 mmoles) of sodium borohydride in 20 ml. of methanol was added dropwise over a period of 20 minutes to a refluxing solution of 500 mg. (1.2 mmoles) of the enol acetate in 20 ml. of methanol and 5 ml. of ether. After heating for three hours, the reaction mixture was decomposed with 3 ml. of concentrated hydrochloric acid and then heated for an additional hour. The mixture was cooled, diluted with 80 ml. of ether, washed with several portions of water, dried over anhydrous sodium sulfate and evaporated. Chromatography of the residue yielded 67 mg. of epicholestanol, m.p. 178–182°, and 357 mg. of cholestanol, m.p. 139–141°.

BERKELEY, CALIFORNIA

(16) Unless otherwise specified, all absorbent used was Merck and Co., Inc., Reagent Aluminum Oxide. Approximately 25 g. of alumina was used per gram of steroid. The solvent sequence employed was hexane, 15% ether (by volume) in hexane and 25% ether in hexane.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY AND THE NATIONAL HEART INSTITUTE]

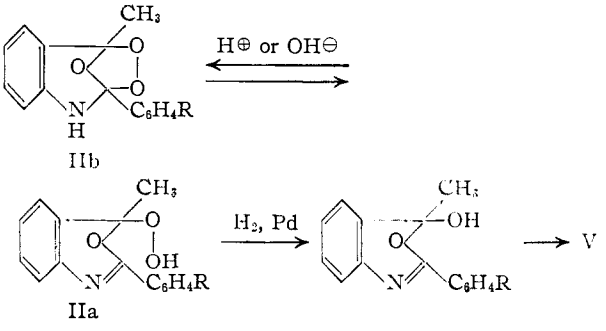
Reductive Cleavages of a Stable Ozonide[1]

BY BERNHARD WITKOP[2] AND JAMES B. PATRICK[2,3]

RECEIVED JULY 9, 1951

The stable ozonide IIa from 2-phenylskatole (I) was studied in its spectral and chemical behavior. The following agents were used for reductive cleavage of the ozonide: hydrogen and palladium, lithium aluminum hydride, sodium boron hydride, alkali metal, phenyl- and *n*-butylmagnesium bromide and methyllithium. For the first time a crystalline ozonide and hydroperoxide (VI), both prepared from the same precursor (I), were correlated *via* their common oxidation product (V) obtained by acid-catalyzed rearrangements from II and VI.

Criegee's recent reinvestigation of certain ozonides has led to a revision of the structure of Hückel's stable "ozonide" from $\Delta^{9,10}$-octalene,[4] established a new course of ozonization for a number of compounds,[5] and thus brought up the question whether the customary formulation of ozonides according to Staudinger[6] is still justified.[7] Especially the ozonides and hydroperoxides derived from 2-(*p*-anisyl)-skatole, [B. Witkop, J. B. Patrick and H. Kissman, Heinrich Wieland Jubilee Volume, *Chem. Ber.*, 85 (1952)] which led to the conclusion that these ozonides are capable of a true *ring-chain tautomerism* (IIa ⇄ IIb:



R = H or OCH_3). All the reactions described in this paper involving the action of acid or base reflect the reactions of the true ozonide (IIb). The reduction with palladium in neutral alcoholic solution starts from the "chain" tautomer IIa leading to the hemiacetal which, lacking the stability of the parent hydroperoxy compound (IIa), isomerizes easily to give *o*-benzaminoacetophenone (V). Also, the decomposition in refluxing benzene without any catalyst is a thermal decomposition of the hydroperoxide tautomer (IIa) involving radical intermediates (formation of diphenyl, etc.).

(1) On the Mechanism of Oxidation. III. Preceding paper in this series: THIS JOURNAL, **73**, 2641 (1951).

(2) National Heart Institute, National Institutes of Health, Bethesda, Md.

(3) Research Corporation Fellow, 1950.

(4) R. Criegee and K. Wenner, *Ann.*, **564**, 9 (1949).

(5) R. Criegee, "Organische Peroxyde, Fortschritte der chemischen Forschung," Vol. I, Springer-Verlag, Berlin, Göttingen, Heidelberg, 1950, pp. 527–530.

(6) Leading literature: A. Rieche, "Alkylperoxyde und Ozonide," T. Steinkopff, Dresden and Leipzig, 1931; L. Long, *Chem. Revs.*, **27**, 437 (1940); A. Rieche, R. Meister and H. Sauthoff, *Ann.*, **553**, 187 (1942).

(7) R. Criegee, European Scientific Notes, Office of Naval Research, London Branch, **4**, 110 (1950).—*Added in proof:* R. Criegee reported on the structure of the ozonide from phenylskatole at the 120th Meeting of the American Chemical Society, New York, N. Y., September 7, 1951, Abstracts 22M. As a result of stimulating discussions with Dr. Criegee, who favored the expression IIa (R = H), we started a more thorough investigation of the spectral and chemical behavior of the