Methylation of the phenolic acid VIII, 1.21 g., in the usual manner with several portions of sodium hydroxide and dimethyl sulfate gave 1.05 g. (81%) of the methoxy acid IX, m.p. 95.5–98°, which was recrystallized three times for analysis; fine white needles, m.p. 98–99°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.16; H, 7.39.

The methoxy acid IX, 1.00 g., was added to 50 g. of polyphosphoric acid (Victor) and stirred while being heated on the steam-bath. After 2 hours the red polyphosphoric acid solution was allowed to cool and ice-water was added. The reaction was extracted with ethyl ether and the yellow ether layer was washed successively with water, saturated potassium bicarbonate solution and water. The ether layer was dried over anhydrous sodium sulfate and concentrated at the steam-bath to an oil which readily crystallized; 410 mg. (46%), m.p. 88–92° (cloudly melt). For analysis the indanone X was distilled at high vacuum, m.p. 88–93°, then recrystallized from cyclohexane in prisms, m.p. 100–100.5°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.88; H, 6.89.

The purified indanone X, 210 mg., 1 g. of activated mossy zinc, 0.4 ml. of water, 0.8 ml. of concd. hydrochloric acid, one drop of glacial acetic acid and 0.4 ml. of toluene were refluxed 51 hours. Approximately every 8 hours, 0.8 ml. of concd. hydrochloric acid was added to the reaction. Ethyl ether and water were then added and the ether layer was separated, washed with water, dried over anhydrous sodium sulfate, concentrated and the oily residue was taken up in 2 ml. of glacial acetic acid. Hydrobromic acid (48%), 0.6 ml., was added and the reaction was refluxed 6 hours. Water and ethyl ether were added and the ether layer was washed successively with saturated sodium bicarbonate solution and water. After drying over sodium sulfate the ether was removed on the steam-bath. The remaining oil, weight 142 mg., crystallized on scratching. Purification of the 7-methyl-5-indanol (VI) was effected by sublimation at the water-pump at 100° followed by recrystallization from petroleum ether (b.p. 30–60°)–dichloromethane and resublimation. The compound, m.p. 83–84°, gave on admixture with the phenol obtained from the acid-catalyzed rearrangement of V, m.p. 82.5–84°. The infrared spectra of the synthetic material and the phenol from V taken in carbon disulfide were identical.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Study of the Hydroxylation of Olefins and the Reaction of Osmium Tetroxide with 1,2-Glycols

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The hydroxylation of trimethylethylene and cyclohexene in *t*-butyl alcohol with hydrogen peroxide in the presence of osmium tetroxide as catalyst has been studied spectroscopically. It has been found that the maximum absorption band due to osmium tetroxide–hydrogen peroxide in *t*-butyl alcohol shifted during hydroxylation from 244 to 286 mμ with trimethylethylene and 288 mμ with cyclohexene. These maxima were also observed to occur when osmium tetroxide was allowed to react in *t*-butyl alcohol with vicinal glycols in the absence of hydrogen peroxide. In the presence of excess hydrogen peroxide these maxima shifted back to the maximum of osmium tetroxide–hydrogen peroxide mixture. It has been concluded that the maxima at 286–288 mμ are due to complexes between osmium tetroxide and the glycols. These complexes were also studied by means of paper chromatography and in the case of ethylene glycol and pinacol they were actually detected and separated.

Introduction

The stereospecificity of hydroxylation of carbon–carbon double bonds with osmium tetroxide alone or in the presence of oxidizing agents such as chlorates or hydrogen peroxide is well known.[4] This fact led Criegee[5] to support the original Wagner–Böeseken[6,7] hypothesis in which osmium tetroxide is used either as a hydroxylation agent or as a catalyst of hydroxylation. Some evidence, however, seems to be at variance with this view. Hofmann[8] reported that the solubility of potassium chlorate in water was increased in the presence of osmium tetroxide, and the oxidation potential of the solution was greater than that of each of the components alone. This seems to indicate that a complex is formed between the chlorate and osmium tetroxide. In a study of the kinetics of hydroxylation of maleic and fumaric acids using osmium tetroxide and chlorates, Zelikoff and Taylor[9] found that the reactive species was a complex between osmium tetroxide and the unsaturated compound, the subsequent step of the formation of the glycol being very rapid. The complex postulated was not entirely in agreement with the Wagner–Böeseken hypothesis.

The hydroxylation of olefins with hydrogen peroxide using osmium tetroxide as a catalyst was originally studied by Milas and co-workers[4] who made the suggestion that the reactive species might be peroxyosmic acid which breaks down to give hydroxyl groups which in turn add to the double bonds to form 1,2-glycols. This view, however, is not entirely consistent with the experimental results of the present investigation. It is well known that osmium tetroxide forms a weak acid, H_2OsO_5, with water, and it is quite possible that in the presence of hydrogen peroxide, which is a stronger acid than water, it may form a highly unstable peroxyosmic acid, H_2OsO_6. This peroxyosmic acid is highly unstable in water and breaks spontaneously and exothermically into

(1) From Ph.D. Thesis, M.I.T., July, 1939.
(2) From Ph.D. Thesis, M.I.T., May, 1955.
(3) U. S. Public Health Service Research Associate, 1957 to date.
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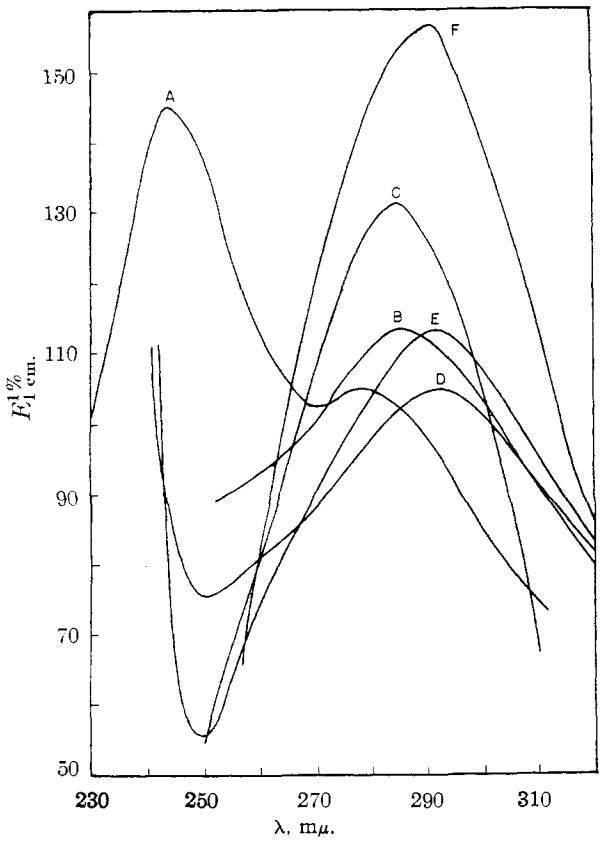


Fig. 1.—Ultraviolet absorption spectra of: (A) equimolecular mixture of hydrogen peroxide and osmium tetroxide in anhydrous *t*-butyl alcohol; (B) reaction of mixture A with trimethylethylene after 1.5 hr.; (C) same as B after 93 hr.; (D) reaction of mixture A with cyclohexene after 1 hr.; (E) same as D after 3 hr.; (F) same as D after 91 hr.

osmium tetroxide and oxygen. However, in *t*-butyl alcohol which is stable to peroxyosmic acid the latter is stable for moderate periods of time. The present communication will describe a spectroscopic study of the hydroxylation of olefins using osmium tetroxide as a catalyst, and the reaction of this catalyst with glycols in the presence or absence of hydrogen peroxide. It will also describe some paper chromatographic experiments which show the detection and separation of complexes formed between glycols and osmium tetroxide.

Discussion

The ultraviolet spectrum of an equimolecular mixture of hydrogen peroxide and osmium tetroxide in anhydrous *t*-butyl alcohol shows a main maximum at 244 mμ and a minor one at 278 mμ (Fig. 1, A). When equimolecular concentrations of trimethylethylene and cyclohexene were allowed to react with the above solution, and the hydroxylation in each case followed spectroscopically, the principal maximum due to osmium tetroxide–hydrogen peroxide mixture gradually disappeared with the formation of a new absorption peak at 286 mμ with trimethylethylene and at 288 mμ with cyclohexene (Fig. 1, B,C,D,E,F). The new maximum was attributed to a complex IV formed between peroxyosmic acid and the olefin. If this were the case then such a maximum should also result when equimolecular proportions of osmium tetroxide and the corresponding glycol were mixed in anhydrous *t*-butyl alcohol in the absence of hydrogen peroxide. The reaction of osmium tetroxide with trimethylethylene glycol is shown in Fig. 2, and the spectra in which the glycols are ethylene glycol and pinacol are recorded in Fig. 3.

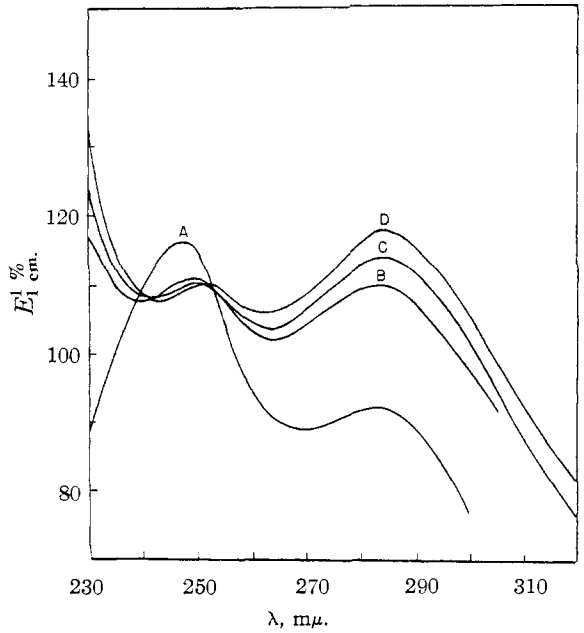


Fig. 2.—Ultraviolet absorption spectra of osmium tetroxide-trimethylethylene glycol complex: (A) after 1 hr.; (B) after 1 day; (C) after 2 days; (D) after 6 days.

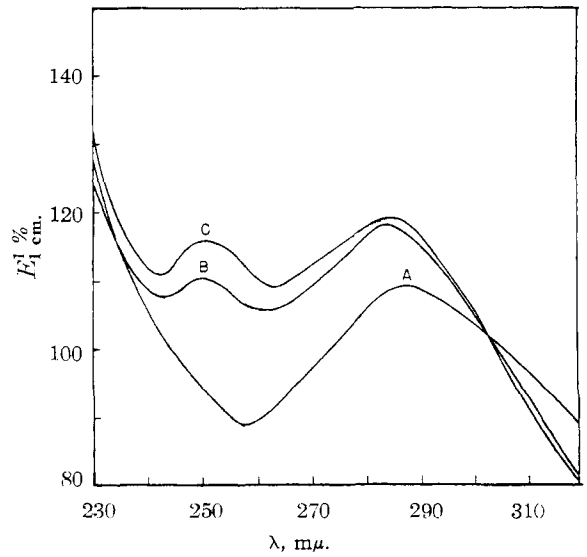
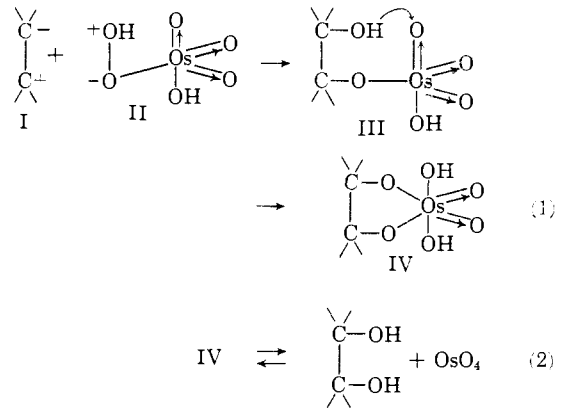


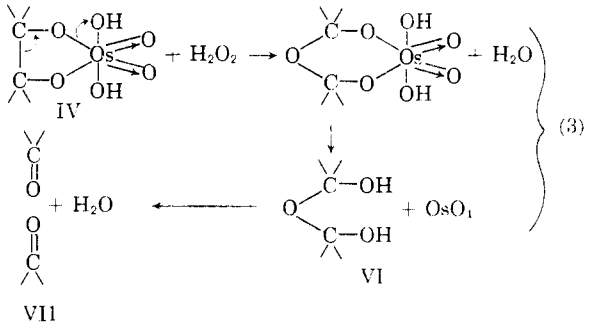
Fig. 3.—Ultraviolet absorption spectra of the osmium tetroxide–glycol complexes: (A) ethylene glycol; (B) trimethylethylene glycol; (C) pinacol.

On the basis of these results the mechanism of hydroxylation of olefins with hydrogen peroxide using osmium tetroxide as catalyst, and the reaction of the latter with 1,2-glycols may be illustrated by the two equations



That reaction 2 is an equilibrium reaction was shown spectroscopically and the fact that the presence of an appreciable amount of water displaces the equilibrium to the right while excess glycol displaces it to the left. Furthermore, since water is more acidic than the glycol, it would tend to form the weak acid, H_2OsO_5.[10-12] Moreover, we have now succeeded to detect and separate the complex IV by means of paper chromatography when ethylene glycol and pinacol were allowed to react with osmium tetroxide. The paper chromatograms of the two complexes showed R_{fs} of 0.96 and 0.95, respectively. It has also been found by this method that 1,6-glycols, like 1,6-hexamethylene diol, undergo oxidation with osmium tetroxide rather than form unstable intermediate addition complexes.

In the absence of water and in the presence of excess hydrogen peroxide the latter oxidizes the intermediate IV as illustrated by the reactions



The oxidation of the complex and the cleavage of the carbon–carbon double bond had been observed chemically by the isolation of the cleavage products. Moreover, the liberation of osmium tetroxide is also shown spectroscopically in Fig. 4 whereby the addition of hydrogen peroxide caused a shift from the maximum due to the complex to that due to osmium tetroxide alone.

Experimental

Preparation of Reagents.—The solvent used in the spectroscopic studies was *t*-butyl alcohol. This was fractionated over calcium hydride and in order to be stable to osmium tetroxide all traces of isobutylene had to be removed by bubbling dry, "prepurified" nitrogen through it for several hours at 40–50° before using. *t*-Butyl alcohol thus prepared was found to be stable for moderate periods of time.

The olefins used were freed from traces of peroxides by shaking them with an aqueous solution of ferrous sulfate for 1 to 2 hr., dried, then fractionated.

The liquid glycols were fractionated under reduced pressure in an atmosphere of nitrogen. Pinacol hexahydrate was fractionated in nitrogen, b.p. 59° (4 mm.), and the solidified distillate recrystallized from anhydrous ethyl ether, m.p. 40°.

All solvents, benzene, *n*-pentane, ligroin (b.p. 94–97°), 1,2-dimethoxyethane, cyclohexane, chloroform and carbon tetrachloride, which were used in connection with paper chromatography, were rigidly purified by standard procedures until they were found to be stable to osmium tetroxide for moderate periods of time.

The solution of hydrogen peroxide in *t*-butyl alcohol was obtained by mixing 1 part of 50% hydrogen peroxide (stabilizer-free) with 10 parts of *t*-butyl alcohol, shaking the mixture with a large excess of anhydrous sodium sulfate and using the clear decanted alcohol layer. This solution is known to contain between 5–8% water and is favorable to hydroxylation, causing only minor cleavage of the double bond.

All spectra were recorded by means of a Beckman spectrophotometer, model DU.

Spectra of Osmium Tetroxide–Hydrogen Peroxide Mixtures in *t*-Butyl Alcohol and Reaction of this Mixture with Cyclohexene and Trimethylethylene.—A suitable concentration of osmium tetroxide in *t*-butyl alcohol for ultraviolet spectra measurements was found to be about $2.54 \times 10^{-4} M$. In the case of the measurements shown in curve A of Fig. 1 the hydrogen peroxide was present in several fold excess over the concentration of osmium tetroxide. For the hydroxylation experiments (Fig. 1, curves B-F) the concentration of osmium tetroxide was the same as above but the concentrations of olefins and hydrogen peroxide were 15-fold excess with cyclohexene and 100-fold excess with trimethylethylene. These concentrations were intentionally used so that osmium tetroxide would always be present in the reactive intermediate state.

Spectra of the Osmium Tetroxide-Glycol Complexes. (a) **Ethylene Glycol.**—To freshly distilled ethylene glycol was added sufficient osmium tetroxide to make a solution of $2.38 \times 10^{-4} M$ osmium tetroxide. The ultraviolet absorption spectrum of this solution showed a single maximum of 288 mμ. The results are plotted in Fig. 3.

(b) **Pinacol.**—In order that the osmium tetroxide–glycol spectra should be as representative as possible, the glycol chosen as an example of a complex with two tertiary hydroxyl groups was pinacol. The molar concentration of pinacol in *t*-butyl alcohol was twice that of the concentration of osmium tetroxide. The absorption spectrum showed two peaks, one at 288 mμ and the other of lower intensity at 244 mμ. The results are plotted in Fig. 3 and compared with plots of ethylene glycol and trimethylethylene glycol.

(c) **Trimethylethylene Glycol.**—In this case equimolecular proportions of osmium tetroxide and freshly distilled trimethylethylene glycol were mixed in *t*-butyl alcohol and the ultraviolet spectrum of the solution taken at appropriate intervals. The results are plotted in Fig. 2. These results show clearly that the intensity of the band at 286 mμ which is attributed to the complex is slowly increasing with time and that of the osmium tetroxide band at 244 mμ is slowly decreasing.

(d) **Oxidation of the Osmium Tetroxide–Trimethylethylene Glycol Complex with Hydrogen Peroxide.**—To the complex of osmium tetroxide and trimethylethylene made under (c) was added a second equivalent of trimethylethylene glycol and to the mixture was added a fivefold excess of hydrogen peroxide in anhydrous *t*-butyl alcohol. Ultraviolet absorption measurements were then made at appropriate intervals and the results plotted in Fig. 4. It may be seen that the intensity of the maximum at 286 mμ attributed to the complex is gradually diminished with time while that attributed to the peroxyosmic acid is increased.

Spectrum of Osmium Tetroxide and Benzene in *t*-Butyl Alcohol.—The ultraviolet absorption spectrum of 1 part of osmium tetroxide to 50 parts of pure benzene in *t*-butyl alcohol was measured at different intervals for 3 days. For the same concentration of osmium tetroxide the spectrum was identical and unchanged even after three days with that of osmium tetroxide alone in *t*-butyl alcohol. Consequently

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no complex was formed between osmium tetroxide and benzene.

Paper Chromatography of Osmium Tetroxide–Glycol Complexes. (1) **Ethylene Glycol–Osmium Tetroxide.**—Osmium tetroxide (0.1646 g.) was dissolved in 5 cc. of freshly distilled ethylene glycol. Immediately a chromatogram was prepared on Whatman No. 1 paper using 4 μl.-131 γ OsO_4 of the solution and another chromatogram with 4 μl. of ethylene glycol. Both were developed with a solvent mixture of benzene (80 vol.) and *n*-pentane (20 vol.). The ethylene glycol–osmium tetroxide complex chromatogram was colorless, but when sprayed with 2% thiourea in 5 *N* hydrochloric acid it developed a pink spot on white background with an R_f of 0.96. When a paper chromatogram is prepared with osmium tetroxide in ligroin and sprayed with the thiourea reagent the paper appears completely white with no pink-colored spots. Apparently the free osmium tetroxide evaporates while the complex remains on the paper. A chromatogram prepared from the ethylene glycol alone was sprayed with 1.5% solution of lead tetraacetate in glacial acetic acid containing 0.1% of acetic anhydride. It showed a white spot due to ethylene glycol which did not move from the place of application.

Another chromatogram was prepared after 4 hr. and the R_f of the complex was found to be the same. Finally, after 20 hr. of standing at room temperature the chromatogram showed again the same R_f for the complex. Moreover, in another chromatogram the complex was oxidized with lead tetraacetate and a white spot appeared on a brown background. This is an additional proof that the glycol was bound to osmium tetroxide.

(2) **Pinacol–Osmium Tetroxide.**—Anhydrous pinacol was dissolved in 1,2-dimethoxyethane to make a solution of 0.273 *M*. To this was added pure osmium tetroxide to make the solution with respect to osmium tetroxide 0.0256 *M*. A paper chromatogram (a) was then prepared with 50 μl.-325 γ OsO_4 and 1614 γ pinacol. This was developed with a mixture of benzene (80 vol.) and *n*-pentane (20 vol.). Two other chromatograms were prepared: (b) with the same solution as a and c with 10 μl.-360 γ of pinacol in absolute ethanol. A fourth chromatogram (d) was also prepared with 50 μl.-272 γ of osmium tetroxide alone in 1,2-dimethoxyethane. Chromatograms c and b were sprayed with lead tetraacetate solution while chromatograms a and d were sprayed with the thiourea reagent. The pinacol in c and the excess pinacol in b failed to move while the complex in a moved to the front and was colorless before spraying and pink colored after spraying with the thiourea reagent. Apparently traces of pink coloration which peared on the spot (d) which failed to move must be due to some other complex or reaction product between osmium tetroxide and 1,2-dimethoxyethane.

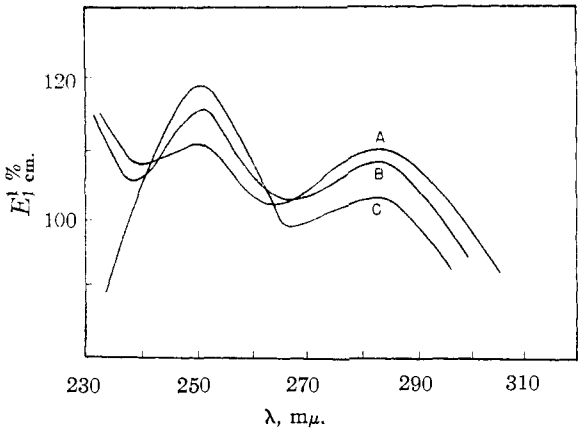

Fig. 4.—Ultraviolet absorption spectra of the osmium tetroxide–trimethylethylene glycol complex upon hydrogen peroxide addition: (A) before hydrogen peroxide addition; (B) 2 hr. after peroxide addition: (C) 1 day after peroxide addition.

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The Semipinacolic Deamination of Certain 1-Alkyl-2-amino-1-phenylethanols

BY HERBERT O. HOUSE AND EDWARD J. GRUBBS[1]

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The ketonic products obtained by the reaction of four 1-alkyl-2-amino-1-phenylethanols with nitrous acid in aqueous acetic acid have been determined. When the alkyl group was methyl, *n*-propyl or isopropyl, the only product detected was the corresponding alkyl benzyl ketone (phenyl migration). When the alkyl group was *t*-butyl, both the corresponding alkyl benzyl ketone and neopentyl phenyl ketone (*t*-butyl migration) were formed.

As part of a general study of the migratory aptitudes of various groups in reactions involving molecular rearrangement, we have studied the semipinacolic deamination of a number of 1,1-disubstituted-2-aminoethanols I in aqueous acetic acid. Data comparing the effects of substitution on the ease of migration of aryl groups in this system are available[2]; these data are in agreement with the generalization that aryl group migration is facilitated by electron-donating substituents. Furthermore, this system is at least sterically similar to the presumed intermediate in the Baeyer–Villiger reaction[3-6] and some parallelism of relative migratory aptitudes is to be anticipated.

In the present study the migratory abilities of the alkyl groups methyl, *n*-propyl, isopropyl and *t*-butyl have been compared with the phenyl group by reaction of the amino alcohols II with nitrous acid. The reaction of the first member IIa of this series has been reported[7] to yield the ketone III (phenyl migration); none of the isomeric ketone IV could be isolated. We have confirmed this result and also demonstrated that the product IIIa contains less than 3% of the ketone IVa. The same result was also obtained with the amino alcohols IIb and IIc. In the latter case, the product III could have contained no more than 1% of the ketone

(1) Eastman Kodak Co. Predoctoral Fellow, 1958–1959.

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