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Acid-Catalyzed Oxidation of Olefins with Selenium Dioxide

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A drastic deviation from the usually accepted reaction path was observed when oxidation of olefins was carried out in acetic acid with selenium dioxide in the presence of concentrated sulfuric acid. Oxidation of cyclohexene gave a mixture of *cis*- and *trans*-1,2-diacetoxycyclohexane. It was shown that in the oxidation of cyclohexene the organoselenium intermediate which produced 3-acetoxy-1-cyclohexene on pyrolysis, is not the intermediate in the present reaction. A study on reaction variables, such as effect of molar ratio of cyclohexene to selenium dioxide, amount of sulfuric acid, and water, reaction time and temperature, was undertaken. The reaction was extended to 1-octene and 1-hexene. A general structure for the organoselenium compound produced in the oxidation of terminal olefins in acetic acid without sulfuric acid, has been proposed. On the basis of our data and some previous concepts a reaction scheme has also been given.

It is generally accepted that oxidation of olefins with selenium dioxide essentially takes place at α position in the most substituted end of the double bond leading to an allylic product that is a function of the solvent used, and order of preference for oxidation is $CH_2 > CH_3$. In a previous paper[1] we reported that addition of two acetoxyl groups to the double bond occurs when the olefins without α-methyl or α-methylene carbon atom are oxidized with selenium dioxide in acetic acid. It is also accepted now that the oxidation follows an ionic path resulting from the electrophilic attack of selenium dioxide or conjugate acid of selenium dioxide on the double bond of the olefin.[2-4] Thus it was thought that addition of a strong acid might either increase the rate of the reaction or change its course by changing the active species. Actually both phenomena were observed. In the oxidation of cyclohexene and 1-octene, the course of the reaction deviated drastically from the generallized path when a small of concentrated sulfuric acid as catalyst was added. We wish to report this new trend in the selenium dioxide oxidation of olefins.

The structure of the organoselenium intermediate resulting from the non-catalytic oxidation of a terminal olefin with selenium dioxide in acetic acid has not been determined. We have proposed a structure for it.

Results and Discussion

Oxidation of Cyclohexene Cyclohexene was selected as a model olefin. Oxidation of cyclohexene has been studied by several researchers. It has been reported that 3-acetoxy-1-cyclohexene is produced in a yield of 48—50% when cyclohexene is treated with selenious acid in acetic anhydride at 80—85°C.[5] 3-Acetoxy-1-cyclohexene is obtained in a yield of 32% together with a trace of 3,6-diacetoxy-1-cyclohexene, when cyclohexene is treated with selenium dioxide in a mixture of acetic acid and acetic anhydride at 80—85°C.[6]

Cyclohexene was oxidized with equimolar amount of selenium dioxide in glacial acetic acid at 110°C for 10 hr in a 200 m*l* glass autoclave in the presence of a small amount of concentrated sulfuric acid to give mainly 1,2-diacetoxycyclohexane in a yield of 32%, as a mixture of *cis* (56%) and *trans* (44%) isomers. Cyclohexenone and cyclohexyl acetate were obtained as minor products. It was interesting to note that no 3-acetoxy-1-cyclohexene was produced and no organoselenium compound could be characterized. Metallic selenium was produced as the final reduced state of the oxidant. This reaction revealed two important features:

i) Addition to the double bond, instead of the allylic oxidation, took place.

ii) *Cis* addition as much as 56% was observed whereas electrophilic additions to cyclohexene molecule are known to give *trans* isomers generally.

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[1] K. A. Javaid, N. Sonoda and S. Tsutsumi, This Bulletin, **42**, 2056 (1969).

[2] J. P. Schaefer, B. Horvath and H. P. Klein, *J. Org. Chem.*, **33**, 2647 (1968).

[3] K. Wiberg and S. D. Neilson, *ibid.*, **29**, 3353 (1964).

[4] J. L. Huguet, *Advan. Chem. Ser.*, **76**, 345 (1968).

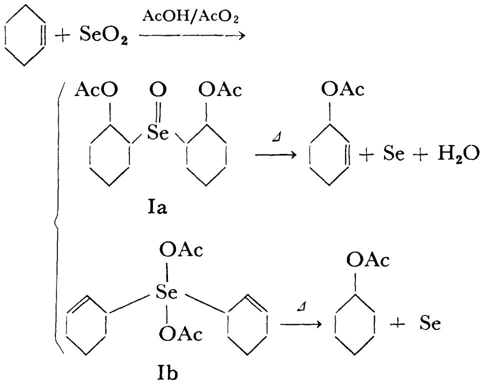
[5] Yu. A. Arbuzov, N. D. Zelinskii and N. I. Shuikin, *Bull. Acad. Sc. U. S. S. R. Classe Sci. Chim.*, 163 (1945).

[6] E. Schwerk and E. Borgwardt, Ger. 584373 (*Chem. Zentr.*, **11**, 3481 (1933)).

Study of the Reaction Variables. The reaction was very sensitive to the change in the molar ratio of olefin to selenium dioxide and the amount of sulfuric acid. Hardly any reaction took place when molar ratio of cyclohexene to selenium dioxide was 3. The yield of 1,2-diacetoxycyclohexene and the rate of the reaction increased with the decrease in the molar ratio of cyclohexene to selenium dioxide. The amount of sulfuric acid was important since it controlled the stereospecificity of the reaction. The increase in the amount of sulfuric acid increased the *trans* isomer (expts. 2, 4). Explanation for this effect is shown in the reaction scheme. Use of the large amount of catalyst resulted in decomposition of the products. The effect of water is also shown in Table 1. The monoacetate formed in each experiment was found to be almost all *cis* isomer, a part of which turns into the *trans* isomer on acid-catalyzed esterification during the reaction. Thus increase in the amount of water increased the *cis* monoacetate and consequently increased the *trans* diacetate (expts. 2 and 7, 4 and 6). The effects of the reaction time and reaction temperature were not so remarkable. The best results were obtained at 110—115°C. The reaction was very slow at 90—100°C and the residue remained in a large amount after distillation of the products at high temperatures. Some results from the study of the different reaction variables are given in Table 1.

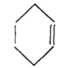
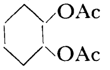
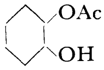
Organoselenium Compounds in the Oxidation of Cyclohexene. We were interested in why the addition of a strong acid changes the reaction path of selenium dioxide oxidation of olefins so much. Two explanations can be given: 1) It is known that oxidation of cyclohexene without sulfuric acid first produces an organoselenium compound which on pyrolysis gives 3-acetoxy-1-cyclohexene.[3] The same organoselenium compound might also have been produced in the present reaction and the subsequent acid catalyzed decomposition may have given 1,2-diacetoxycyclohexene. 2) Addition of strong acid changed the active species at an early stage of the reaction, leading to different products.

A detailed study of organoselenium compounds was undertaken. The organoselenium compound from cyclohexene, responsible for the allylic oxidation products, was prepared by the method given by Arbuzov *et al.*[5] and purified by column chromatography. Wiberg and Neilsen[3] proposed two structures (Ia and Ib) for the compound emphasizing the probability in favor of Ia. The infrared spectrum of the compound purified by column chromatography showed it to be an acetate and absorptions for –OH or C=C were not found. NMR spectrum indicated the presence of –$\overset{|}{\text{C}}$HOAc. No absorption peak for the olefinic proton could be detected. These spectroscopic data confirm the structure Ia.



To investigate whether Ia is also an intermediate in the acid-catalyzed oxidation of cyclohexene or not, the compound was decomposed in acetic acid containing a small amount of sulfuric acid under similar conditions as those applied for the acid-catalyzed oxidation of cyclohexene. A large amount of metallic selenium was produced. Among the products, 3,6-diacetoxy-1-cyclohexene and a small amount of 1,2-diacetoxycyclohexane could be detected. The former product was considered to be formed by further oxidation of 3-acetoxy-1-cyclohexene. The discrepancies in the nature of the products, and the percentage composition

TABLE 1. OXIDATION OF CYCLOHEXENE

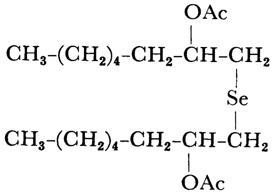
	Reaction conditions						Products %		Isomers % of diacetate	
	 mol	SeO_2 mol	H_2SO_4 *ml*	H_2O *ml*	Time hr	Temp. °C			*cis*	*trans*
1	0.146	0.072	0.27	—	9	110	2.5	—	—	—
2	0.098	0.072	0.27	—	9	110	20.0	3.6	50	50
3	0.098	0.098	0.27	—	9	110	30.0	2.0	50	50
4	0.098	0.072	0.18	—	9	110	21.0	2.0	56	44
5	0.098	0.072	0.13	2.5	9	110	18.0	4.0	44	56
6	0.098	0.072	0.18	5.0	12	110	15.2	6.8	37	63
7	0.098	0.072	0.27	18.0	9	110	14.5	9.0	25	75

of the stereoisomers obtained from the direct acid-catalyzed oxidation of cyclohexene and acid-catalyzed decomposition of the organoselenium compound from cyclohexene, lead us to the conclusion that the compound Ia is not the intermediate in the acid-catalyzed oxidation of cyclohexene, and that the addition of sulfuric acid has changed the active species at an early stage of the reaction.

Oxidation of 1-Octene. On the basis of the results obtained from the oxidation of cyclohexene, studies were extended to some terminal olefins such as 1-octene and 1-hexene to investigate the scope of the reaction. Oxidation of 1-octene with equimolar amount of selenium dioxide in acetic acid at 115°C for 10 hr in the presence of concentrated sulfuric acid as a catalyst, gave 1,2-diacetoxyoctane (35%) and a trace of 1-acetoxy-2-octene. When 1-octene was oxidized with selenium dioxide in a mixture of acetic acid and acetic anhydride without sulfuric acid, an organoselenium compound was produced as a major product with a small amount of 1-acetoxy-2-octene. Thermal decomposition of the organoselenium compound gave again 1-acetoxy-2-octene. The acid-catalyzed decomposition of the organoselenium compound in acetic acid containing a small amount of sulfuric acid under similar conditions to those subjected to the acid-catalyzed oxidation of 1-octene, also produced 1-acetoxy-2-octene as a major product and a small amount of 3-acetoxy-1-octene. The result indicates that the organoselenium compound also, is not the intermediate in the acid-catalyzed oxidation of 1-octene.

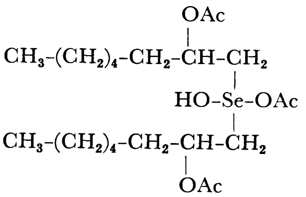
Organoselenium Compounds in the Oxidation of 1-Octene. Recently oxidation of 1-octene was studied by bubbling air through the reaction mixture, and the formation of two organoselenium compounds IIa and IIb with a small amount of 1-acetoxy-2-octene was reported.7)

$$CH_3\text{-}(CH_2)_5\text{-}CH{=}CH_2 + SeO_2 + AcOH \xrightarrow{\text{Air}}$$



$$CH_3\text{-}(CH_2)_4\text{-}CH_2\text{-}CH(OAc)\text{-}CH_2\text{-}Se\text{-}CH_2\text{-}CH(OAc)\text{-}CH_2\text{-}(CH_2)_4\text{-}CH_3$$

IIa



$$CH_3\text{-}(CH_2)_4\text{-}CH_2\text{-}CH(OAc)\text{-}CH_2\text{-}Se(OH)(OAc)\text{-}CH_2\text{-}CH(OAc)\text{-}CH_2\text{-}(CH_2)_4\text{-}CH_3$$

IIb

Decomposition of IIa and IIb in acetic acid containing a small amount of sulfuric acid under similar conditions to those used for the acid-catalyzed oxidation of 1-octene produced again 1,2-diacetoxyoctane. Reaction conditions and stoichiometric calculations indicate that this may be formed from IIb. We assume from the results that in the direct formation of 1,2-diacetoxyoctane from 1-octene, active species resembling IIb may be involved, but IIb can not be considered as the major intermediate in the acid-catalyzed oxidation of 1-octene because of the difference in the yield of the products from the two cases. We can also conclude that organoselenium compound formed in the oxidation of 1-octene is different when (a) air is bubbled, and (b) air is not bubbled. The decomposition in (a) leads to diacetate formation while that in (b) leads to allylic oxidation products. No structure has been assigned to the organoselenium compound resulting from the non-catalytic oxidation of the terminal olefins. In the present work it was purified by column chromatography and its structure III was assigned on the basis of its infrared and NMR spectral data and the results of thermal and acid-catalyzed decompositions. Thermal decomposition of III should be facile and may proceed through a cyclic transition state to give the allylic oxidation product. (Scheme 1)

The effect of air is not understood except that bubbling of it reduced the selenium deposition.7) It was thought that the following reaction takes place.

$$Se \xrightarrow{\text{Air}} SeO$$

$$\text{III} \longrightarrow \text{IIa} + SeO_2$$

Oxidation of 1-Hexene. Almost the same results as obtained in the oxidation of cyclohexene or 1-octene, except that considerable amounts of allylic oxidation products were obtained along with the addition products, were observed. Thus, oxidation of 1-hexene with an equimolar amount of selenium dioxide in acetic acid at 105°C for 10 hr in the presence of a small amount of concentrated sulfuric acid produced 1,2-diacetoxyhexane (35%), 3-acetoxy-1-hexene, (12%) and 1-acetoxy-2-hexene (5%). Identification of the products was carried out by infrared and NMR spectral analyses and GLC.

In order to compare the reaction with a known one, 1-hexene was oxidized with selenium dioxide following the procedure of Guillemonat8) to give mainly the organoselenium compound which on pyrolysis and acid-catalyzed decomposition in acetic acid separately produced a mixture of 1-

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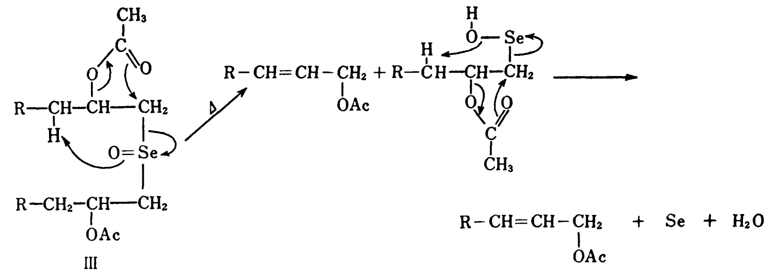
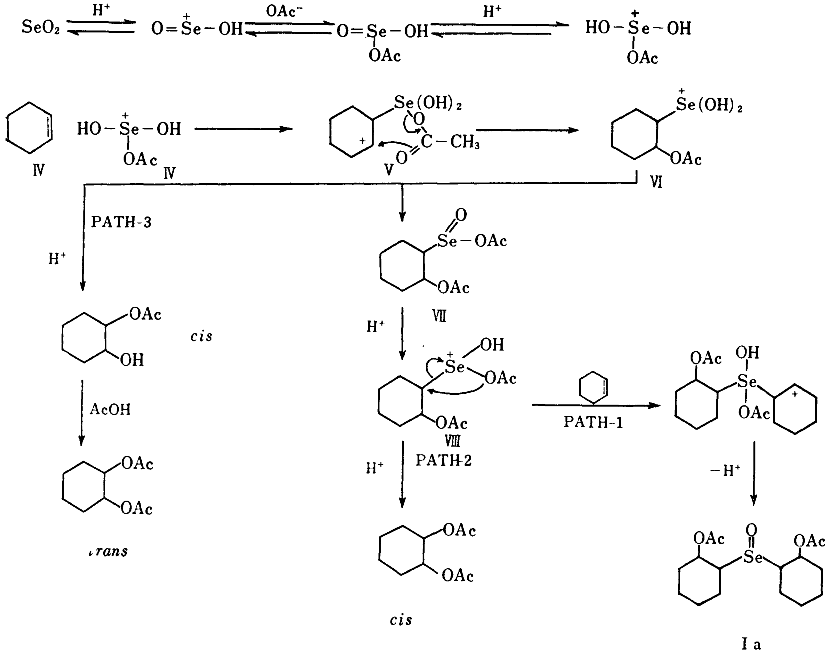
7) K. Takaoka and Y. Toyama, *Nippon Kagaku Zasshi*, **89**, 618 (1968).

8) A. Guillemonat, *Ann. Chim.* (Paris), **11**, 143 (1939).



(Scheme 1)



(Scheme 2)

acetoxy-2-hexene and 3-acetoxy-1-hexene.

Reaction Scheme. Schaefer *et al.*[2] suggested a reaction mechanism for the oxidation of olefins. Olson[9] gave a modified mechanism for the oxidation of ethylene. In view of the basic concepts postulated by these workers, a reaction scheme may be given from the consideration of the data presented above and our previous results indicating the *exo-cis* addition of acetoxyl groups to the double bond of norbornene molecule.[1]

According to the reaction scheme (Scheme 2), if no catalyst the reaction will follow path 1 to give there is the organoselenium compound which consequently leads to the allylic oxidation products. In the presence of a small amount of sulfuric acid as the catalyst the reaction will mainly deviated to path 2, whereas the large amount of the catalyst will tend to change the reaction path to 3. The production of the *cis* isomers may be attributed to the interamolecular acetoxylation through a cyclic transition state (VIII) formed by the addition of sulfuric acid as a strong proton donor. The scheme also explains the production of monoacetates as primary products.

Experimental

All the reactions were conducted in a 250 m*l* graduated glass autoclave with a mechanically operated stainless steel stirrer, which can be operated up to a pressure of 15 kg/cm^2. Infrared spectra were taken with a Shimadzu IR-27C spectrophotometer. The proton NMR spectra were taken on a Japan Electron Optics Lab. JNM C-60 spectrometer in deuteriochloroform with TMS as an internal standard. For mass spectral analysis, a Hitachi RMU-60 mass spectrometer was employed with the electron beam energy at 80 eV.

Acid-catalyzed Oxidation of Cyclohexene. A typical example is given here to cover the general reaction procedure. Selenium dioxide (11 g) was suspended in 50 m*l* of glacial acetic acid in the glass autoclave, cyclohexene (8 g) was diluted with a small amount of

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9) D. H. Olson, *Tetrahedron Lett.*, **1966**, 2053.

acetic acid and transferred to the autoclave, 0.18 m*l* of concentrated sulfuric acid was added as a catalyst and the total volume was made up to 150 m*l* with acetic acid. The autoclave was heated at 110°C for 10 hr with stirring preventing the settling of selenium dioxide. The color of the reaction mixture changed from yellow to brown and ultimately to black due to the deposition of metallic selenium. After the reaction was over, selenium was filtered off and acetic acid was removed by vacuum distillation. The distillate collected at 40°C/3 mmHg, was found to be a mixture of cyclohexyl acetate and cyclohexenone by GLC. The second fraction boiling at 95°C/3 mmHg was characterized as 1,2-diacetoxycyclohexane (5.5 g). NMR spectrum: τ 5.1 (multiplet, 2H, $\rangle$CH–OAc), 7.95 (singlet, 6H, $-OCOCH_3$), 7.9—8.8 (multiplet, 8H, ring methylenes).

Non-catalytic Oxidation of Cyclohexene. The procedure given by Arbuzov *et al.*[5] was followed to give a small amount of 3-acetoxy-1-cyclohexene and an organoselenium compound mainly as residue. The residue was divided into three parts. One part was subjected to pyrolysis in a distillation flask at 250°C under the reduced pressure of 20 mmHg to give 3-acetoxy-1-cyclohexene and a small amount of 3,6-diacetoxy-1-cyclohexene. Second part of the residue (about 10 g) was dissolved in 120 m*l* of acetic acid in the glass autoclave, and thermal decomposition was carried out at 110°C for 8 hr in the presence of 0.18 m*l* of concentrated sulfuric acid. Metallic selenium was filtered off and acetic acid was removed by vacuum distillation. The distillate at 95—100°C/3 mmHg was characterized as a mixture of 3,6-diacetoxy-1-cyclohexene, *trans* 1,2-diacetoxycyclohexane and an unknown product. Silica gel column chromatography was employed for the purification of the organoselenium compound. The residue (about 1 g) was diluted with 4 m*l* of *n*-hexane and transfered to a 35 cm × 2.5 cm column containing 40 g of silica gel in 80 m*l* of *n*-hexane. The eluents used were *n*-hexane, a mixture of 50% *n*-hexane and 50% benzene, pure benzene and a mixture of 95% benzene and 5% ether. On the basis of its infrared and NMR spectra and the results of thermal and acid-catalyzed decompositions, the structure Ia was confirmed. NMR: τ 5.2 (multiplet, 2H, $\rangle$CHOAc), 7.1 (multiplet, 2H, $\rangle$CH–SeO–), 7.95 (singlet, 6H, $-OCOCH_3$), 7.9—8.8 (multiplet, 16H, ring methylenes).

Acid-catalyzed Oxidation of 1-Octene. Selenium dioxide (8 g) was suspended in 50 m*l* of acetic acid in the glass autoclave and 1-octene (8 g) was added. The total volume was made up to 140 m*l* with acetic acid and 0.18 m*l* of concentrated sulfuric acid was added as a catalyst. The reaction was carried out at 115°C for 10 hr. After metallic selenium was removed by filtration, acetic acid was distilled off under the reduced pressure. The distillate boiling at 105—110°C/3 mmHg was almost pure 1,2-diacetoxyoctane (6.5 g). Redistillation of the fraction gave pure 1,2-diacetoxyoctane, 107°C/3 mmHg. NMR: τ 5.1 (multiplet, 1H, $-CHOAc$), 5.9 (multiplet, 2H, $\rangle CH_2OAc$), 7.95 (singlet, 6H, $-OCOCH_3$), 8.2—9.5 (multiplet, 13H, $-C_6H_{13}$).

Non-catalytic Oxidation of 1-Octene. Selenium dioxide (5 g) was suspended in 120 m*l* of glacial acetic acid and 15 m*l* of acetic anhydride in the glass autoclave and 1-octene (10 g) was poured in. The autoclave was heated at 100—105°C for 8 hr. No deposition of metallic selenium was observed. The solvents and the unreacted 1-octene were removed by vacuum distillation. A small amount of product was obtained at 55°C/3 mmHg and a dark brown residue remained. The product was identified as 1-acetoxy-2-octene by GLC. The residue was pyrolysed in a distillation flask to give 1-acetoxy-2-octene. The acid-catalyzed decomposition of the residue in acetic acid at 115°C for 8 hr in the presence of 0.18 m*l* of concentrated sulfuric acid gave 1-acetoxy-2-octene and a small amount of 3-acetoxy-1-octene. The organoselenium compound was purified by silica gel column chromatography. The method applied was the same as that used for the purification of the organoselenium compound (Ia) from cyclohexene. Structure III was assigned on the basis of its infrared and NMR analyses. NMR spectrum: τ 5.15 (multiplet, 2H, $\rangle$CHOAc), 7.25 (doublet, 4H, $-CH_2-SeO-$), 7.95 (singlet, 6H, $-OCOCH_3$), 8.2—9.3 (multiplet, 26H, $-C_6H_{13}$).

Acid-catalyzed Oxidation of 1-Hexene. Selenium dioxide (5.5 g) was suspended in 50 m*l* of acetic acid in the glass autoclave and 1-hexene (4 g) was added. The total volume was made up to 140 m*l* with acetic acid and 0.14 m*l* of concentrated sulfuric acid was added as a catalyst. Oxidation was carried out at 105°C for 10 hr with stirring. The deposited metallic selenium was filtered off and acetic acid was removed by vacuum distillation. The fraction boiling at 40—45°C/3 mmHg was found to be a mixture of 1-acetoxy-2-hexene (5%) and 3-acetoxy-1-hexene (12%) by GLC. The second distillate collected at 85°C/2 mmHg was found to be 1,2-diacetoxyhexane (35%). Its structure was confirmed by comparison with an authentic sample. NMR spectrum: τ 5.1 (multiplet, 1H, $-CHOAc$), 5.9 (multiplet, 2H, $-CH_2OAc$), 7.95 (singlet, 6H, $-OCOCH_3$), 8.2—9.2 (multiplet, 9H, $-C_4H_9$).

Non-catalytic Oxidation of 1-Hexene. The procedure of Guillemonat[8] was followed. Organoselenium compound was the major product. Pyrolysis of the compound at 250°C/23 mmHg in a distillation flask gave a mixture of 1-acetoxy-2-hexene and 3-acetoxy-1-hexene in the ratio 3 to 1. The acid-catalyzed decomposition of the organoselenium compound (10 g) in 120 m*l* of acetic acid containing 0.14 m*l* of concentrated sulfuric acid at 105°C for 8 hr gave 1-acetoxy-2-hexene and 3-acetoxy-1-hexene in the ratio 2 to 1.

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