BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (10), 3022—3026 (1978) [Vol. 51, No. 10

Metal-catalyzed Organic Photoreactions. The Photooxidation of Olefins in the Presence of Uranyl Acetate[1)]

Eigoro Murayama and Tadashi Sato*

Department of Applied Chemistry, Waseda University, Ookubo 3, Shinjuku-ku, Tokyo 160

(Received March 15, 1978)

The photooxidation of olefins in pyridine in the presence of uranyl acetate afforded β-hydroxy hydroperoxides. It was confirmed by spectroscopic studies and isotope-incorporation experiments that (1) the stereochemistry of the hydroxyl and hydroperoxyl groups in the β-hydroxy hydroperoxides was *trans*, (2) the hydroxyl group was added to the less substituted carbon of the double bond, and (3) the oxygen atom in the hydroxyl group originated mainly from the water molecule, while the oxygen atoms in the hydroperoxyl group originated mainly from molecular oxygen. From these results, we proposed a reaction scheme of: (i) the formation of the hydroxyl radical from water by uranyl acetate-catalyzed photolysis, (ii) the addition of the hydroxyl radical to the double bond, (iii) the combination of the resulted radical with molecular oxygen, and (iv) the hydrogen abstraction of the peroxyl radical to give the product. The scheme was further supported by the photoreaction of 2-methyl-2-butene with bromotrichloromethane in the presence of uranyl acetate, which afforded 3-bromo-3-methyl-2-butanol as the major product.

The dye-sensitized photooxidation and the autoxidation are two major types of the photooxidation of olefins, and they have been interpreted as involving the reaction of singlet oxygen and the initiation by a radical respectively.[2)] Recently several papers on photooxidation through novel types of mechanism have been published. Photooxidations sensitized by dicyanoanthracene,[3)] α-diketones,[4)] or Lewis acids[5)] are some examples.

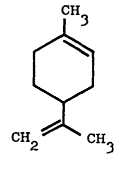
In the course of our study of the metal-catalyzed organic photoreactions,[6)] we found that the photooxidation of olefins in pyridine in the presence of uranyl acetate proceeded in a way quite different from the oxidation processes known so far.

Results and Discussion

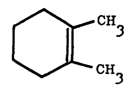
Solutions of limonene (**1**), 1,2-dimethylcyclohexene (**2**), or 2-methyl-2-butene (**3**) in pyridine, all containing an equivalent amount of uranyl acetate (dihydrate), were irradiated with Pyrex-filtered light while oxygen was bubbled through, and the products were separated on preparative TLC (silica gel). β-Hydroxy hydroperoxides, **4**, **5**, and **6**, were isolated in a fairly pure state in 14, 8, and 12% yields respectively. The yields of these products, as determined by NMR analyses of the crude reaction mixtures, amounted to 32, 11, and 18% respectively. The compounds **4** and **6** were further purified by vacuum distillation. The structures **4**, **5**, and **6** were assigned on the basis of the spectroscopic and elemental analyses[7)] and the following chemical processes.

Upon the hydrogenation on palladium–charcoal, the β-hydroxy hydroperoxides, **4**, **5**, and **6**, gave 1,2-diols, **7a**, **8**, and **9** respectively, while they afforded C–C bond cleavage products (**10** from **4**, **11** from **5**, and acetone and acetaldehyde from **6**) upon thermolysis or decomposition on silica gel. With a view to elucidating the stereochemistry of **7a**, we hydrogenated a stereoisomeric mixture of *trans*-diol **12**,[8)] and then isolated **7a** and **7b** on a preparative VPC. We assigned the stereochemistry of these isomers as indicated in view of the $W_H=6$ Hz value of H_a in **7a**, in contrast with the J values of 12 and 4 Hz (doublet of a doublet) for the corresponding proton in **7b**. The reduction product from **4** was identical with **7a**, thus establishing the stereochemistry of **4** to be as shown. The diols, **8** and **9**, were identical with authentic samples prepared by known methods.[9)]

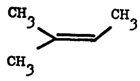
The positional assignments of the substituents in **6** were deduced from the carbon-NMR analyses. While the chemical shifts of the secondary carbons (C_1) in compounds **6** and **9** were fairly close to each other (δ 70.5 for **6** and δ 74.2 for **9**), the signal of the tertiary carbon (C_2) in **6** appeared at a lower field (δ 85.1) than that of the corresponding carbon in **9** (δ 73.4). These observations would definitely support the tertiary



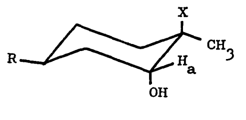
1



2

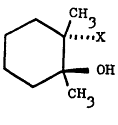


3



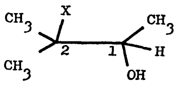
4: R = >— , X = OOH

7a: R = >— , X = OH



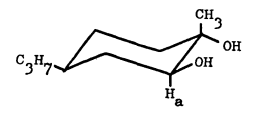
5: X = OOH

8: X = OH

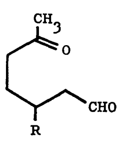


6: X = OOH

9: X = OH

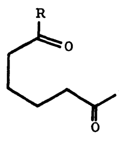


7b



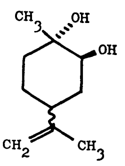
10: R = >—

20: R = H



11: R = CH3

21: R = H



12 (isomers)

hydroperoxide structure for **6**, and the same regiochemistry was also postulated with compound **4**. Subramanyam *et al.* prepared several β-hydroxy hydroperoxides including **6**, which indicated spectroscopic data very close to ours.[10)]

In order to gain an insight into the genuine character of the present reaction, the irradiated materials from **1** and **2** were directly treated with silica gel (to decompose β-hydroxy hydroperoxides) and the products were analyzed by a preparative VPC. A keto aldehyde, **10**, and a ketone, **13**, probable decomposition products of the β-hydroxy hydroperoxides from **1** at the 1,2- and 8,9-positions, were obtained from **1** in 26 and 2% yields respectively, along with three by-products, **12**, **14**, and **15** in 1, 1, and 3% yields respectively. Similarly, **11** was obtained in a 48% isolated yield from **2**, along with several by-products (**16**, **17**, and others; see Reference 2; total yield, 9%). In view of our previous observations,[2)] it is evident that these by-products from **1** and **2** are formed through the radical-initiated oxidation. We have also reported that the allyl hydroperoxides, such as **18** and **19** are characteristic products of the singlet-oxygen oxidations of **1** and **2**, but these products were negligible in the present reactions. No observable amounts of any other products were isolated, but we have not examined whether the remainder becomes unextractable polymeric substances or remains intact as the original starting materials. The starting materials, even if they remained at the end of the reaction, could not be detected because they escaped during the work-up procedure of removing the pyridine solvent.

The possibility that the present oxidation might proceed through the uranyl acetate-catalyzed oxidation by singlet oxygen was ruled out in the following way. When solutions of **1** and **2** in *t*-butyl alcohol–water (1: 1) or in pyridine, containing rose bengal as a sensitizer, were irradiated with a tungsten lamp, oxidation products were obtained with a product distribution typical of singlet-oxygen oxidation.[2)] Under these conditions, however, no catalytic effect of uranyl acetate was observed. It was also shown by the experiment with **2** that the present oxidation is not affected by a radical scavenger (tri-*t*-butylphenol).

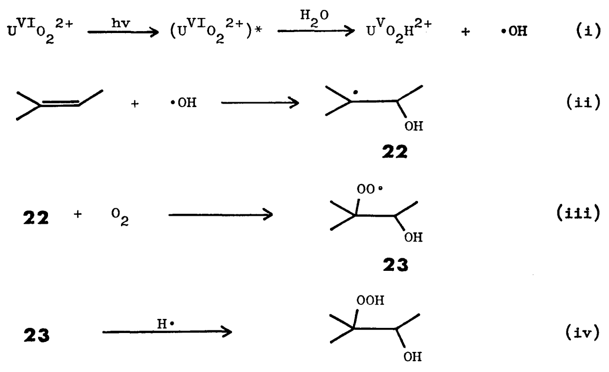
The same type of reaction seems to proceed with 1-methylcyclohexene and cyclohexene, because these olefins, under the same conditions of irradiation and succeeding decomposition on silica gel, afforded a keto aldehyde, **20**, and a dialdehyde, **21**, in 20 and 6% yields respectively. The yield of **21** was low because of the apparent polymerization during the work-up procedure.

Uranyl chloride in *t*-butyl alcohol–water (1: 1) also catalyzed the present reaction, although the competitive radical-initiated oxidation process became appreciable under these conditions. However, no appreciable amounts of any products were observed when either of the metal compounds, light, or oxygen was lacking.

With a view to clarifying the reaction mechanism, the sources of the oxygen atoms in the product, **6**, were determined in the following way. The product, **6**, obtained by using oxygen-18 labelled water or molecular oxygen, was directly injected into a gas chromatograph-mass spectrometer, after which the isotope contents incorporated into acetone and acetaldehyde, the thermolyzed products from **6** in the gas chromatograph, were determined mass-spectrometrically. The results are shown in Table 1. Assuming that no oxygen migration occurs during the thermolysis step of **6**, as has been proposed for the fragmentation of α-hydroperoxy acid,[11)] it was concluded that the oxygen atoms in the hydroperoxyl group originated mainly (90%) from molecular oxygen, while the oxygen atom in the hydroxyl group originated, in major part (67%), from the water molecule. We could scheme the major course of the reaction as: (i) the formation of the hydroxyl radical from water by uranyl acetate-catalyzed photolysis; (ii) the addition of the hydroxyl radical to the olefin so as to afford the more stable intermediate; (iii) the combination of the preceeding radical, **22**, with molecular oxygen, and (iv) the hydrogen abstraction of **23** to give the product (Scheme 1).

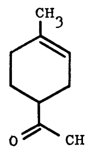
Table 1. Incorporation of oxygen-18 into acetone and acetaldehyde

Condition	^{18}O in acetone (atom % excess)	^{18}O in acetaldehyde (atom % excess)
$^{18}O_2$ (30 atom % excess)–$UO_2(OAc)_2 \cdot 2H_2O$	27	7
O_2–$UO_2(OAc)_2 \cdot H_2{}^{18}O$ (30 atom % excess)	5	20

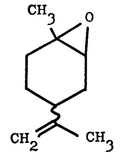


Scheme 1.

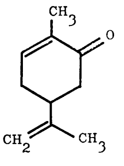
Although the stereo- and regio-chemistry of the present reaction are consistent with the scheme, the fact that the reaction under a lack of oxygen gives no observable products needs further consideration, because some products from the radical **22** (for instance, an alcohol, **24**, through the hydrogen abstraction) should be produced in view of the proposed scheme. The problem could be interpreted in the following way. First, we can assume that Step i is reversible and that, in the absence of oxygen, the back reaction is too fast to allow the hydroxyl radical to be involved in the further reaction. In the presence of oxygen, however, the back reaction might be inhibited due to the oxidation by oxygen of the low-valent uranium compound, and the hydroxyl radical could well survive to be involved in the next step. The reaction shown in Step i has been suggested by Burrows and Kemp[12)] in the uranyl compound-catalyzed photolyses of water, although they failed to detect the hydroxyl radical, supposedly because of the fast back reaction. Alternatively, we can assume that the hydroxyl radical produced in Step i could reversibly add to the olefin, but in the absence of any appropriate substance to trap the radical **22** effectively, the whole reaction does not proceed because of the back reaction in Step i. Presumably the second interpretation is preferable because we observed that the hydroxyl radical could be brought into the reaction, even in the absence of oxygen, as long as a suitable substance to trap the radical **22** is present. We found that bromotrichloromethane serves for this purpose. When a solution of **3** in pyridine containing uranyl acetate and bromotrichloromethane was irradiated with Pyrex-filtered light, two bromohydrins, **25** and **26**, were obtained as a 3: 1 mixture in a 18% yield, along with the addition product, **27**, in a 12% yield. When the irradiation was carried out in the absence of uranyl acetate, **27** was the sole product.[13] The structure of **25** was assigned on the basis of elemental and spectroscopic analyses, and by oxidizing the bromohydrin to α-bromoketone, **28**. The structures **26**[14] and **27**[13] were confirmed by comparing the compounds with authentic samples prepared by known procedures. We found that the ratios of **26**/**25** were independent (≈0.3) of the wavelength of the working light, the amounts of bromotrichloromethane and water, and the presence or absence of some additives, while the ratios of **27**/(**25**+**26**) changed from 0 to 1.2 depending upon the reaction conditions. Although the detailed results will be reported elsewhere, it can be suggested from these observations that **25** and **26** are formed *via* a common intermediate (probably a uranyl-substrate complex). A normal type of the addition of HOBr to the olefin, **3**, is known to occur so as to give **26** selectively;[14] therefore, the abnormal way of addition in the present reaction would be another support for the proposed scheme. Recently we found a photooxidation of olefins in the presence of iron(III) chloride to give chlorinated ketones. These reactions have been speculated[15] as proceeding in a way similar to that shown in the scheme proposed in this paper.



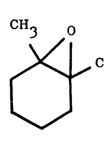
13



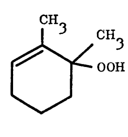
14 (isomers)



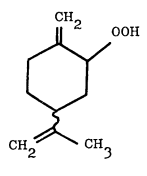
15



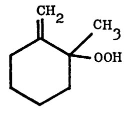
16



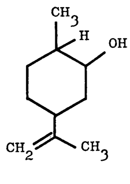
17



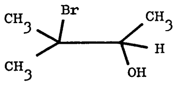
18 (isomers)



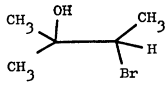
19



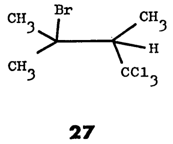
24



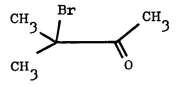
25



26



27



28

Experimental

General Procedures. The instrumentation was the same as has been described previously.[16] The carbon NMR spectra were determined in a $CDCl_3$ solution on a JEOL JNM-FX 100 spectrometer; the chemical shifts are represented in δ values relative to the internal TMS standard. The isotope incorporations were determined on a Hitachi RMU-6M mass spectrometer equipped with a gas chromatograph.

Unless otherwise stated, a pyridine solution (2—6 mmol, 0.02 M) of olefin containing an equivalent amount of uranyl acetate (dihydrate) was irradiated in Pyrex-glass test tubes with a high-pressure mercury vapor lamp (Ushio UM 452 (450 W)) for 10—90 min while oxygen was bubbled through. After the irradiation, the pyridine was removed *in vacuo* and the reaction products were extracted from the residue with carbon tetrachloride. The extract was filtered, and the solvent was removed *in vacuo*. The residual substance was treated as has been indicated below.

Materials. *a) Unhydrous Uranyl Acetate*: Commercially available uranyl acetate dihydrate (500 mg) was heated at 140 °C under reduced pressure for 30 min, and the resulting yellow powder (459 mg) was used directly for the reactions. *b) Oxygen-18 Labelled Water*: Commercially available $H_2{}^{18}O$ (96.5 atom% excess, Merck Sharp and Dohme Canada, Ltd., Lot No. B-863) was diluted with ordinary water to a concentration of 30 atom % excess of ^{18}O. *c) Oxygen-18 Labelled Molecular Oxygen*: Commercially available $^{18}O_2$ (70 atom % excess, B.O.C. Ltd.) was diluted with ordinary oxygen to a concentration of 30 atom % excess of ^{18}O.

*Photooxidation of **1**.* When the crude oil from 272 mg of **1** was purified by preparative TLC (silica gel, chloroform), **4** was isolated (52 mg, 14%); this was then further purified by vacuum distillation. Bp 45—55 °C (≈10^{-5} mmHg). IR (neat), 3350, 3080, 2930, 1642, 1450, 1378, 1035, 890, and 840 cm^{-1}. NMR (CCl_4), δ 1.22 (3H, s), 1.70 (3H, s), 3.88 (1H, bs), 4.64 (2H, bs), and 4.6—5.9 (2H, bs, shifts upon dilution). Found:[7] C, 64.75; H, 9.11%. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%.

When the crude oil was dissolved in chloroform and passed through a silica-gel column (10 cm), an oil was obtained from which five products, **10**, **12**, **13**, **14**, and **15**, were subsequently isolated by preparative VPC. The IR and NMR spectra of **10**[17] and **13**[18] were identical with those of the authentic samples obtained by the known methods. The IR and NMR spectra of **14** and **15** corresponded to those previously reported.[2] The IR and NMR spectra of **12** were identical with those of the samples described below.

*Photooxidation of **2**.* The crude oil from 330 mg of **2** was dissolved in 20 ml water and then washed with hexane. After copper(II) sulfate (3.5 g) had been added to the aqueous layer, the solution was shaken with chloroform. The extract (Extract A) was dried (Na_2SO_4), and the solvent was removed *in vacuo*. When the residual substance was purified by preparative TLC (silica gel, chloroform), **5** was isolated (38 mg, 8%). The NMR analysis indicated that the compound contained a small amount of **11**. **5**: in a state containing a small amount of **11**, IR (neat), 3380, 2935, 1372, 1120, and 1060 cm^{-1}. NMR (CCl_4), δ 1.21 (3H, s), 1.27 (3H, s), and 1.2—1.6 (m).

The Extract A obtained from 220 mg of **2** was applied on a silica-gel column (5 cm) and then eluted with chloroform. Upon removing the solvent *in vacuo* from the eluate, crystals of **11** were isolated in a pure state (137 mg, 48%). Mp 24—26 °C (lit,[19] mp 41—42.5 °C). NMR (CCl_4), δ 1.42 (4H, m), 2.03 (6H, s), and 2.33 (4H, dist. t). The IR spectrum was identical with that previously reported.[20]

From the hexane layer, the by-products[2] (40 mg) were obtained (9% total yield).

The same result was obtained (46% yield of **11**) when the reaction was carried out in the presence of tri-*t*-butylphenol (262 mg).

Photooxidation of 3. When the crude oil from 420 mg of **3** was distilled under reduced pressure, **6** was isolated in a pure state (59 mg, 12%). Bp 47—48 °C ($\approx 10^{-5}$ mmHg). IR (neat), 3320, 2980, 1387, 1110, and 835 cm^{-1}. NMR (CCl_4), δ 1.04 (3H, s), 1.07 (3H, d, J=6.4 Hz), 1.16 (3H, s), 3.92 (1H, q, J=6.4 Hz), and 4.8—7.7 (2H, bs, shifts upon dilution). Carbon-NMR ($CDCl_3$), δ 17.3 (q, J=126 Hz), 17.6 (q, J=127 Hz), 21.6 (q, J=126 Hz), 70.5 (d, J=145 Hz), and 85.1 (s). Found:[7] C, 51.20; H, 10.23%. Calcd for $C_5H_{12}O_3$: C, 49.98; H, 10.07%.

Isotope-incorporation experiments were carried out in the following way. A solution of **3** (14 mg) in unhydrous pyridine (10 ml), containing unhydrous uranyl acetate (68 mg) and $H_2{}^{18}O$ (30 atom% excess, 372 mg), was irradiated for 30 min while ordinary oxygen was bubbled through. The crude oil, obtained by means of the work-up described above, was directly injected into the gas chromatograph-mass spectrometer.

Hydrogenation of 4. A solution of **4** (15 mg) in ethanol (5 ml), containing 10% palladium-charcoal (10 mg), was stirred under an hydrogen atmosphere (1 atm) for two days. The oil which remained after the catalyst and solvent had been removed was almost pure **7a**. Preparative VPC gave a pure sample of **7a** which showed spectroscopic data identical with those of the sample described below.

Hydrogenation of 5. A solution of **5** (22 mg) in ethanol (2 ml) was stirred under a hydrogen atmosphere (1 atm) for 20 h in the presence of 10% palladium-charcoal (5 mg). An NMR analysis indicated that the oil remaining after the work-up was a mixture of **8** and **11** (1:1). The separation was accomplished on a preparative VPC. The IR and NMR spectra of **8** were identical with those of an authentic sample.[9]

Hydrogenation of 6. The hydrogenation in the way described above gave a pure sample of **9**. The IR and NMR data were identical with those of an authentic sample.[9] Carbon-NMR ($CDCl_3$), δ 17.7 (q, J=125 Hz), 22.6 (q, J=125 Hz), 26.5 (q, J=125 Hz), 73.4 (s), and 74.2 (d, J=142 Hz).

Preparation of 7a. A solution of a stereoisomeric mixture of **14**[21] (200 mg) in *t*-butyl alcohol-water (1:1 by volume, 20 ml), also containing 0.5 M-sulfuric acid (0.2 ml), was stirred at room temperature for 16 h. The reaction mixture was then poured into a saturated aqueous solution of sodium bicarbonate (40 ml) and shaken with chloroform. The extract was dried (Na_2SO_4), and the solvent was removed *in vacuo*. The residual substance was distilled to give a stereoisomeric mixture of **12** (141 mg).[8,22] Bp 95—97 °C (10 mmHg). A solution of the diol **12** obtained above (82 mg) in ethanol (5 ml), containing 10% palladium-charcoal (10 mg), was stirred under a hydrogen atmosphere (1 atm) for 17 h. Preparative VPC after the distillation (94—96 °C (4 mmHg)) gave two stereoisomers, **7a** and **7b**, in a pure state. **7a**: IR (CCl_4), 3650 cm^{-1}. NMR (CCl_4), δ 0.91 (6H, d, J=6 Hz), 1.19 (3H, s), and 3.57 (1H, bs, W_H=6 Hz). **7b**: IR (CCl_4), 3420 cm^{-1}. NMR (CCl_4), δ 0.91 (6H, d, J=6 Hz), 1.11 (3H, s), and 3.52 (1H, dd, J=12 and 4 Hz).

Thermolysis of 4. A solution of **4** (40 mg) in benzene (1 ml) was refluxed for 30 min, and then the solvent was removed *in vacuo*. From the IR, NMR, and VPC analyses, the major part of the residual oil was found to be **10**.,

Thermolysis of 5. A solution of **5** (16 mg) in benzene (2 ml) was refluxed for 1 h, and then the solvent was removed *in vacuo*. From the NMR analysis, the residual oil was found to be **11**.

Thermolysis of 6. A small amount of **6** was injected into a gas chromatograph-mass spectrometer (temperature of the injection port: 260 °C), and the decomposition products were directly analyzed on the mass spectrometer. The two products detected were identified as acetone and acetaldehyde from the mass spectra and the retention times on the VPC.

Photooxidation of 1-Methylcyclohexene. The crude oil from 288 mg of 1-methylcyclohexene was chromatographed on a silica-gel column (chloroform), and **20** (77 mg, 20%) was isolated. The IR and NMR spectra of **20** were identical with those of an authentic sample.[23]

Photooxidation of Cyclohexene. The crude oil from 246 mg of cyclohexene was treated in the way described above; the product thus obtained, **21** (39 mg, 6%), was accompanied by a small amount of a polymerization product of **21**. IR (neat), 2830, 2720, and 1720 cm^{-1}. NMR (CCl_4), δ 1.4—1.8 (4H, m), 2.2—2.8 (4H, m), and 9.57 (2H, t, J=1.5 Hz).

Photoreaction of 3 with Bromotrichloromethane. A solution of **3** (0.5 g) in pyridine (360 ml), containing uranyl acetate (3.1 g) and bromotrichloromethane (2.9 g), was irradiated with Pyrex-filtered light from a high-pressure mercury vapor lamp (Ushio UM 1000 (1 kW)) for 1 h. After the irradiation, the pyridine was removed *in vacuo*. The reaction products were extracted from the residue with chloroform, and the extract was passed through a Florisil column (6 cm) in a chloroform solution. The eluate was washed with a saturated aqueous solution of copper(II) sulfate, and dried over Na_2SO_4, and the solvent was removed *in vacuo*. The residual substance was dissolved in hexane, and the solution was shaken with a cold 2% aqueous solution of sodium bicarbonate. The aqueous layer was shaken with cold chloroform, the chloroform solution was dried (Na_2SO_4), and the solvent was removed *in vacuo* to give a yellow oil (220 mg). From NMR analysis, the oil was found to be a mixture of **25** and **26** (3:1). The vacuum distillation (bp 40—41 °C (9 mmHg)) did not accomplish the complete separation of the two isomers, and so spectroscopic and elemental analyses were carried out on the mixture. Subtracting the spectra of **26**, which was prepared in a pure state according to the reported method,[14] the spectra of **25** were as follows: IR (neat), 3400, 2975, 1455, 1373, 1112, 942, and 702 cm^{-1}. NMR (CCl_4), δ 1.21 (3H, d, J=6 Hz), 1.68 (3H, s), 1.72 (3H, s), 3.04 (1H, bs), and 3.55 (1H, q, J=6 Hz). Found:[24] C, 36.63; H, 6.58%. Calcd for $C_5H_{11}OBr$: C, 35.95; H, 6.64%.

The hexane layer was dried over Na_2SO_4, and the hexane was removed *in vacuo*. The brown oil was mainly **27** identical with an authentic sample.[13] The yield of **27** was 12%, as determined by NMR analysis, using 1,1,2,2-tetrachloroethane as an internal reference.

Oxidation of 25. The oxidation of the mixture of **25** and **26** obtained above (40 mg) with a Jones reagent was carried out according to the reported procedure.[14a)] α-Bromoketone **28** was obtained, accompanied by unchanged **26**; the spectra of **28** were obtained by subtracting those of **26**. IR[25)] (neat), 2975, 1710, 1372, 1360, 1138, and 1104 cm^{-1}. NMR[26)] (CCl_4), δ 1.81 (6H, s) and 2.36 (3H, s).

References

1) Preliminary report: E. Murayama and T. Sato, *Tetrahedron Lett.*, **1977**, 4079.

2) T. Sato and E. Murayama, *Bull. Chem. Soc. Jpn.*, **47**, 715 (1974), and references cited therein.

3) J. Eriksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99**, 6455 (1977).

4) N. Shimizu and P. D. Bartlett, *J. Am. Chem. Soc.*, **98**, 4193 (1976).

5) D. H. R. Barton and R. K. Haynes, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 2065.

6) T. Sato, S. Yoshiie, T. Imamura, K. Hasegawa, M. Miyahara, S. Yamamura, and O. Ito, *Bull. Chem. Soc. Jpn.*, **50**, 2714 (1977), and references cited therein.

7) Errors in the elemental analyses were inevitable due to a slight decomposition during the distillation and contamination by a trace amount of the pyridine solvent.

8) M. Sumimoto, T. Suzuki, and T. Kondo, *Agr. Biol. Chem.*, **38**, 1061 (1974).

9) The two diols, **8** and **9**, were prepared from **2** and **3** respectively, according to the method which gives *trans*-1,2-cyclohexanediol from cyclohexene; A. Roebuck and H. Adkins, *Org. Synth.*, Coll. Vol. III, 217 (1965).

10) V. Subramanyam, C. L. Brizuela, and A. H. Soloway, *J. Chem. Soc., Chem. Commun.*, **1976**, 508, and private communication from Dr. Subramanyam.

11) W. Adam, A. Alzérreca, Ju-Chao Liu, and F. Yany, *J. Am. Chem. Soc.*, **99**, 5768 (1977).

12) H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, **3**, 139 (1974).

13) M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

14) a) D. R. Dalton and V. P. Dutta, *J. Chem. Soc., B*, **1971**, 85; b) D. R. Dalton, V. P. Dutta, and D. G. Jones, *J. Am. Chem. Soc.*, **90**, 5498 (1968).

15) E. Murayama, A. Kohda, and T. Sato, *Chem. Lett.*, **1978**, 161.

16) T. Sato, K. Tamura, K. Maruyama, O. Ogawa, and T. Imamura, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 779.

17) S. Kataoka and Y. Hamada, *Bull. Agr. Chem. Soc. Jpn.*, **20**, 223 (1956).

18) E. E. Lutz and G. M. Baily, *J. Am. Chem. Soc.*, **86**, 3889 (1964).

19) H. Adkins and C. Scanley, *J. Am. Chem. Soc.*, **73**, 2854 (1951).

20) "The Aldrich Library of Infrared Spectra," Aldrich Chemical Co., (1970), p. 195E.

21) T. Sato and E. Murayama, *Bull. Chem. Soc. Jpn.*, **47**, 1207 (1974).

22) W. F. Newhall, *J. Org. Chem.*, **29**, 185 (1964).

23) M. Barbier and M. F. Hügel, *Bull. Soc. Chim. Fr.*, **1961**, 951.

24) Errors in elemental analyses were inevitable due to the contamination by a trace amount of 2-bromopyridine.

25) L. Blanco, P. Amice, and J. M. Conia, *Synthesis*, **1976** 194.

26) R. A. Cox and J. Warkentin, *Can. J. Chem.*, **50**, 3242 (1972).