TABLE I

REACTION OF N-BROMOSUCCINIMIDE WITH VARIOUS SECONDARY ALCOHOLS[a]

Alcohol	Moles of Alcohol: Moles of NBS[b]	Proton Acceptor	Products			
			Ketone	%	Brominated ketone	%
2-Propanol	1:1	None	None		Bromoacetone	30
2-Propanol	1:1	$CaCO_3$	Acetone[c]	Trace	Bromoacetone	30
2-Propanol	1:1	Pyridine	Acetone	60	None	
Cyclohexanol	1:1	Pyridine	Cyclohexanone	61	None[d]	
Phenyl methyl carbinol[e]	1:1	Pyridine	Acetophenone	65	None	
Phenyl methyl carbinol	1:2	None	None		Phenacyl bromide	45
Ethyl lactate	1:1	None	Ethyl pyruvate	10	Ethyl bromopyruvate	20
Ethyl lactate	1:1	$CaCO_3$	Ethyl pyruvate	58	Ethyl bromopyruvate	19
Ethyl lactate	1:1	Pyridine	Ethyl pyruvate	42	None	
Ethyl 2-hydroxybutyrate[e]	1:1	Pyridine	Ethyl 2-ketobutyrate[f]	50	None	

[a] Carbon tetrachloride was the solvent in all reactions. When pyridine was used as the proton acceptor the temperature was held between 60–70°; the reactions with 2-propanol are exothermic; the others were refluxed from 4–8 hr. [b] *N*-Bromosuccinimide. [c] Isolated as the 2,4-dinitrophenylhydrazone; m.p. 126°. [d] H. Schmid and P. Karrer[8] reported the direct bromination of cyclohexanone with *N*-bromosuccinimide. The oxidation in this case is extremely rapid. [e] Ref. 7. [f] B.p. 66–67° (16 mm.); m.p. of phenylhydrazone 191°. Van der Sleen, G., *Rec. trav. chim.*, **21**, 234 (1902).

chloride on a steam bath the residue was diluted with ether, washed successively with saturated aqueous calcium chloride and 5% hydrochloric acid, dried over anhydrous magnesium sulfate, and fractionated. The yield of ethyl pyruvate was 42%. No ethyl bromopyruvate was formed.

Oxidation of cyclohexanol. A mixture of 5 g. (0.05 mole) of cyclohexanol, 8.9 g. (0.05 mole) of *N*-bromosuccinimide, and 3.9 g. (0.05 mole) of pyridine in 50 ml. of dry carbon tetrachloride was heated on a steam bath at 60–70° for 4 hr. The mixture was allowed to stand overnight at room temperature, filtered, and the filtrate fractionated through a short column. The yield of cyclohexanone, b.p. 148–150°, was 3 g. or 61%. The melting point of its 2,4-dinitrophenylhydrazone was 162°.

Oxidation of ethyl 3-chlorolactate. A mixture of 7.67 g. (0.05 mole) of ethyl 3-chlorolactate, 8.9 g. (0.05 mole) of *N*-bromosuccinimide, and 75 ml. of carbon tetrachloride was refluxed for 3 hr. The mixture was filtered, the filtrate dried over anhydrous sodium sulfate, and distilled. The yield of ethyl chloropyruvate[9] boiling at 74–75° (8 mm.) was 5.5 g. (72%).

Attempted oxidation of β-hydroxyisovaleronitrile. A mixture of 9.9 g. (0.1 mole) of β-hydroxyisovaleronitrile, 17.8 g. (0.1 mole) of *N*-bromosuccinimide, 7.9 g. (0.1 mole) of pyridine in 100 ml. of carbon tetrachloride reacted spontaneously as evidenced by the rise in temperature of the reaction mixture. After the initial temperature increase had abated the mixture was kept at 60 to 70° for 2 hr. The mixture was then treated as described for ethyl lactate. Distillation yielded isobutyraldehyde, a small amount of 2-oxo-*iso*-valeric acid and a larger fraction which, judged by its boiling point (217–218°), may have been the dimer of β-oxoisovaleronitrile described by Moritz.[10]

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(9) J. Parrod, *Compt. rend.*, **218**, 599 (1944).

(10) E. Moritz, *J. Chem. Soc.*, **39**, 23 (1881).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

Reactions of Hydrogen Peroxide. II. A Novel Use of Selenium Dioxide as Catalyst for the Ring Contraction of Cycloalkanones to Cycloalkanecarboxylic Acids[1]

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Oxidative ring contractions of cycloheptanone, cyclohexanone, and cyclopentanone to cyclohexane-, cyclopentane-, and cyclobutanecarboxylic acids in 34, 32, and 23% yields, respectively, have been obtained with hydrogen peroxide and selenium dioxide as catalyst.

The use of selenium dioxide as catalyst for the oxidation of acrolein to acrylic acid has recently been described.[1] In a further investigation of the action of selenium dioxide in the presence of hydrogen peroxide, the oxidation of cycloheptanone, cyclohexanone, and cyclopentanone was investigated. It was anticipated that the cyclic ketones might undergo the well-known reaction with selenium dioxide giving alpha-diketones, with hydrogen peroxide serving merely to oxidize selenium metal back to the dioxide. It was found, however, that along with other competing reactions, all three ketones underwent oxidative ring contraction to cyclohexane-, cyclopentane- and cyclobutanecarboxylic acids in 34, 32, and 23% yields, respectively. Adipic acid was identified as another prod-

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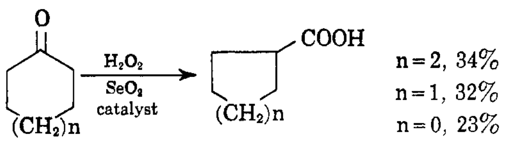
(1) For the preceding article in this series see C. W. Smith and R. T. Holm, *J. Org. Chem.* 22, 746 (1957).



uct of the reaction of cyclohexanone by esterification of the non-volatile acids formed. No investigation was made of the other higher boiling products from cyclopentanone or cycloheptanone, however.

The reactions were best carried out in tertiary butyl alcohol solution at 80° for about 2 hr. using equimolar quantities of ketone and hydrogen peroxide and about 2 mole % of selenium dioxide catalyst. In the case of cyclohexanone, the solvent-free mixture of products was separated into neutral and acidic fractions which were distilled separately. About 15% of starting ketone was recovered, along with just a trace of higher boiling neutral material. Distillation of the acidic portion gave cyclopentanecarboxylic acid as the only volatile product. Similar results were obtained with cycloheptanone.

No attempt was made to separate the mixture from cyclopentanone oxidation into acidic and neutral portions. Instead, direct distillation gave cyclobutanecarboxylic acid as the only volatile product.

The ring contraction of a 6-membered ring cyclic ketone to a cyclopentanecarboxylic acid has been observed before[2] in a β-diketone system that was incorporated in a dispiro compound; the Faworskii rearrangement of α-chlorocyclohexanone to cyclopentanecarboxylic acid is, of course, well known.[3] The contraction of a 5-membered ring to a 4, however, as in the case of cyclopentanone, appears to be rather unusual. For example, the Faworskii rearrangement of α-chlorocyclopentanone to cyclobutanecarboxylic acid was not observed.[3]

That the α-diketone is probably not an intermediate in the rearrangement was indicated by the failure of 1,2-cyclohexanedione to give any cyclopentanecarboxylic acid when subjected to the action of a catalytic amount of selenium dioxide and hydrogen peroxide. Aside from this evidence, little is known about the mechanism of the ring contraction. One can postulate, however, that selenium dioxide (selenious acid) is oxidized by hydrogen peroxide to selenic acid and that in some unknown manner the latter promotes the oxidative ring contraction.

EXPERIMENTAL[4]

Selenium dioxide catalyzed oxidation of cyclohexanone. To a stirred solution of 300 g. (3.0 moles) of 34% hydrogen peroxide and 5 g. (0.045 mole) of selenium dioxide in 1000 ml. of tertiary-butyl alcohol at 80° was added dropwise 294 g. (3.0 moles) of cyclohexanone. The reaction mixture was held at 80° by cooling with an ice bath during the hour required for addition. After completion of the addition, the reaction maintained temperature at 80° for 1.5 hr. with very little cooling being required. At that point, red selenium metal was deposited and the mixture was allowed to cool to room temperature overnight. After removal of selenium by filtration, distillation was carried out with a 40-tray Oldershaw column[4a] to remove the alcohol-water azeotrope. When the head temperature reached 85°, distillation was halted and the residue was cooled and poured into 750 ml. of ether. The ether solution was extracted successively with 20% potassium carbonate solution and water and dried over anhydrous sodium sulfate. Distillation of the ether solution gave 45 g. of recovered cyclohexanone, b.p. 153–155°, and only 5 g. of residual neutral product. The carbonate extract was acidified and extracted with ether. The ether solution was water-washed, dried over sodium sulfate, and concentrated to low volume on the steam bath. Distillation of the residue through a 1 × 50 cm. glass-helices packed column gave 77 g. (27% yield based on unrecovered cyclohexanone) of cyclopentanecarboxylic acid, b.p. 87–89° (2–3 mm.). n_D^{20} 1.4534; m.p. 3–4°; reported values: b.p. 215–216°[5]); n_D^{20} 1.4532;[6] m.p. 4–5°.[5]

Esterification of the 98 g. of residue from the above distillation with 1-butanol afforded 19 g. (5% yield based on unrecovered ketone) of butyl cyclopentanecarboxylate, b.p. 58–59° (1 mm.), n_D^{20} 1.4394; reported[7]) b.p. 95–97° (15 mm.). Thirteen grams of crude dibutyl adipate, b.p. 112–115° (1 mm.), n_D^{20} 1.4402, was also obtained.

Anal. Calcd. for butyl cyclopentanecarboxylate, $C_{10}H_{18}O_2$: C, 70.5; H, 10.6; saponification equiv., 170. Found: C, 70.3; H, 10.6; sapon. equiv., 172.

Anal. Calcd. for dibutyl adipate, $C_{14}H_{26}O_4$: C, 65.1; H, 10.1; sapon. equiv., 130. Found: C, 64.6; H, 9.9; sapon. equiv., 137.

The *acid chloride* of cyclopentanecarboxylic acid was prepared from 30 g. of the acid by refluxing with 50 ml. of thionyl chloride for 1 hr. The mixture was distilled to give 30 g. (86%) of product, b.p. 160–162°; reported[8] b.p. 160–162°.

The *amide* was prepared from a portion of the acid chloride by reaction with concentrated ammonium hydroxide. It was recrystallized from water and sublimed at 125° (2 mm.), m.p. 177–178°; reported[9] m.p. 178–179°.

Oxidation of cyclopentanone. The oxidation of 126 g. (1.5 moles) of cyclopentanone was carried out exactly as described above for cyclohexanone. The crude reaction mixture was filtered to remove selenium metal and distilled through the 50 cm. packed column to give 35 g. of cyclobutanecarboxylic acid (23% yield based on cyclopentanone charged; no attempt made to recover unreacted ketone), b.p. 74–76° (2.5 mm.); n_D^{20} 1.4446; reported[10], b.p. 195–196°, n_D^{20} 1.4434. The residue from the distillation amounted to 60 g. of dark viscous oil; it was not investigated.

The *amide* was prepared as above from crude acid chloride, m.p. 151–152°; reported[11]) m.p. 152–153°. The melt-

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[2] C. Mannich, *Ber.*, **74B**, 1007 (1941).

[3] M. Mousseron, R. Jacquier, and A. Fontaine, *Compt. rend.*, **231**, 864 (1950); R. B. Loftfield, *J. Am. Chem. Soc.*, **73**, 4707 (1951).

[4] All melting points are corrected.

[4a] C. F. Oldershaw, *Ind. Eng. Chem., Anal. Ed.* **13**, 265 (1941).

[5] A Faworskii and V. Bozhovskii, *J. Russ. Phys. Chem. Soc.*, **46**, 1092 (1914).

[6] S. S. Nametkin and A. K. Ruzhentzova, *J. Russ. Phys. Chem. Soc.*, **46**, 1540, (1914).

[7] M. Mousseron and R. Jacquier, *Compt. rend.*, **229**, 374 (1949).

[8] E. Haworth, and H. W. Perkin, *J. Chem. Soc.*, **99** (1894).

[9] D. Venus-Danilova, *J. Gen. Chem. U.S.S.R.*, **6**, 697 (1936).

[10] G. J. Östling, *J. Chem. Soc.*, 473 (1912).

[11] W. H. Perkin, *J. Chem. Soc.*, 958 (1894).

ing point was not depressed when mixed with an authentic sample of cyclobutanecarboxamide, m.p. 151–152°.[12]

The *anilide* was prepared from crude acid chloride, m.p. 111–112° after recrystallization from benzene-petroleum ether; reported[13] m.p. 111°.

Oxidation of cycloheptanone. The oxidation of 100 g. (0.89 mole) of cycloheptanone (Aldrich Chemical Co. n_D^{20} 1.4608) was carried out exactly as above. After removal of solvent the crude product was separated into neutral and acidic fractions which were distilled separately through a 1 × 50 cm. packed column. The neutral portion afforded 18.5 g. of recovered ketone, b.p. 92° (50 mm.), n_D^{20} 1.4610, and 6 g. of non-volatile residue. The acidic fraction gave 32 g. (34% based on unrecovered cycloheptanone) of cyclohexanecarboxylic acid, b.p. 63–67° (<1 mm.), m.p. 25–29°; reported values: b.p. 223.5°, m.p. 29°.[14]

Anal. Calcd. for $C_7H_{12}O_2$: Neut. equiv., 128. Found: Neut. equiv., 128.

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[12] We are indebted to Prof. Henry Rapoport of the University of California for a generous sample of authentic acid chloride from which this amide was prepared.

[13] M. Freund and E. Gudeman, *Ber.*, **21**, 2692 (1888).

[14] J. S. Lumsden, *J. Chem. Soc.*, 90 (1905).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

Reactions of Hydrogen Peroxide. III. Tungstic Acid Catalyzed Hydroxylation of Cyclohexene in Nonaqueous Media

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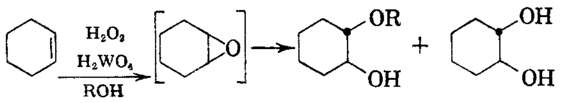
A novel conversion of an unsaturated linkage to its corresponding α-glycol monoether has been realized. Thus, tungstic acid catalyzed hydroxylations of cyclohexene with 90% hydrogen peroxide in methanol, ethanol, and 2-propanol have given the corresponding 2-alkoxycyclohexanols in 70, 41, and 21% yields, respectively. *Trans*-1,2-cyclohexanediol was also obtained in each case. With tertiary butyl alcohol as solvent no glycol monoether was found and the major product was the diol; also isolated in this case was 1-cyclopentenecarboxaldehyde, formed by the acid catalyzed rearrangement of the intermediate peroxide, 2-hydroperoxycyclohexanol. Isolation of the latter (as its cyclic ketal with acetone) represents a significant addition to the understanding of the cleavage of olefins to aldehydes with hydrogen peroxide.

The literature contains many reports on the use of osmium tetroxide, performic acid, and peracetic acid for the hydroxylation of a variety of unsaturated materials. Tungstic acid has also been described as an effective hydroxylation catalyst, particularly when employed in aqueous or acetic acid solution.[1]

Mugdan and Young[1] reported poor yields in the hydroxylation of cyclohexene in tertiary butyl alcohol solution, and also noted that loss of peroxide due to decomposition to water and oxygen was troublesome when such solvents as acetone, dioxane, or methanol were used.

In the present study, we have subjected cyclohexene to the action of hydrogen peroxide and tungstic acid catalyst in methanol, ethanol, 2-propanol, tertiary butyl alcohol, and acetone. Using 90% hydrogen peroxide with methanol as solvent, a 70% yield of 2-methoxycyclohexanol was realized along with a 16% yield of *trans*-1,2-cyclohexanediol.

This direct conversion by hydrogen peroxide of an unsaturated linkage to its corresponding α-glycol monoether has apparently not been reported before. Evidence that the reaction is a general one for lower molecular weight primary and secondary alcohols was obtained by the formation of 2-ethoxycyclohexanol and 2-isopropoxycyclohexanol, respectively, when ethanol and isopropyl alcohol were substituted for methanol.



$R = CH_3$: 70% 16%
$R = C_2H_5$: 41% 36%
$R = i\text{-}C_3H_7$: 21% 44%
$R = t\text{-}C_4H_9$: 0% 50%

The glycol monoethers are undoubtedly formed by the acid catalyzed action of alcohol, in competition with water (from the hydrogen peroxide), on the intermediate epoxide.[2] It was not surprising to find, therefore, that the most polar alcohol, methanol,[3] gave the highest yield of α-glycol monoether and the lowest yield of α-glycol.

While ethanol and isopropyl alcohol provided smaller, but nevertheless substantial amounts of hydroxy ether, none of the latter was observed when *tert*-butyl alcohol was employed as solvent. Either the tertiary alcohol failed to react with the intermediate epoxide, or any tertiary ether that might have been formed was unstable in the acidic medium and underwent conversion to α-glycol and isobutylene.[4] From the reaction in *tert*-butyl alcohol

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[1] I. Bergsteinson, U.S. Patent 2,373,942 (Apr. 17, 1945); M. Mugdan and D. P. Young, *J. Chem. Soc.* 2988 (1949).

[2] Epoxy compounds have been isolated as intermediates in the hydroxylation of other unsaturated materials with tungstic acid catalyst (unpublished results, Shell Development Co.).

[3] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, N. Y., 1950, p. 256.

[4] T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, **28**, 1186 (1936).