SSC_4H_9, 629-45-8; $C_4H_9SeC_4H_9$, 14835-66-6; $C_4H_9SeC_6H_5$, 28622-61-9; β-$C_{10}H_7SS$-β-$C_{10}H_7$, 5586-15-2.

Acknowledgment.—We gratefully acknowledge the support of this research by the National Science Foundation through Research Project GP-4505 with the University of Florida.

A Mechanistic Study of 1,2-Glycol Cleavage with Nickel Peroxide

RYUSEI KONAKA*[1] AND KAZUO KURUMA

Shionogi Research Laboratory, Shionogi & Co., Ltd.,
Fukushima-ku, Osaka, Japan

Received July 13, 1970

It has previously been found by Nakagawa, Igano, and Sugita[2] that nickel peroxide[3] is a useful oxidant for the oxidative cleavage of 1,2-diols and related compounds, as are periodic acid, lead tetraacetate, phenyliodoso acetate, and sodium bismuthate. In connection with mechanistic studies[4] on nickel peroxide oxidations reported recently, which explained the oxidative action of nickel peroxide in terms of its having characteristic abilities for both hydrogen abstraction and OH radical donation, we have investigated the mechanism of the unusual oxidative cleavage of 1,2-diols with nickel peroxide.

The fact that the oxidation of *meso*-hydrobenzoin with nickel peroxide (50°, 1 hr) gives benzaldehyde in 85% yield, while that of pinacol (70°, 3 hr) gives acetone in 61% yield[2] indicates that elimination of the hydrogen on the α position of the 1,2-glycol is not necessary in the oxidative cleavage of 1,2-diols with nickel peroxide. In order to establish this, the isotope effects in the oxidative cleavage of *meso*-1,2-diphenyl-1,2-dideuterioethane-1,2-diol and *meso*-2,3-dideuteriobutane-2,3-diol were examined, since the oxidation of a monohydric alcohol with nickel peroxide begins with hydrogen abstraction at the α position of the alcohol ($k_H/k_D = 7.4$ on the oxidation of benzhydrol).[4] The values of the pseudo-first-order reaction rate constants determined by a thermoanalytical technique[5] are shown in Table I. The data suggest that no isotope effect occurs in either reaction within the experimental error.

TABLE I

RATE CONSTANTS FOR THE OXIDATION OF 1,2-GLYCOLS AND RELATED COMPOUNDS WITH NICKEL PEROXIDE

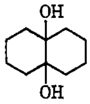
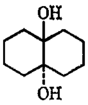
Substrate	Registry no.	Temp, °C	k, sec^{-1}
$(C_6H_5C(OH)H-)_2$	579-43-1	31	4×10^{-2}
$(C_6H_5C(OH)D-)_2$	28795-90-6	31	5×10^{-2}
$(CH_3C(OH)H-)_2$	5341-95-7	1	6.8×10^{-4}
$(CH_3C(OH)D-)_2$	28795-91-7	1	9.1×10^{-4}
$C_6H_5CH_2CH(OH)C_6H_5$	614-29-9	30	5.2×10^{-5}
$C_6H_5CH(OH)C_6H_5$	91-01-0	30	5.3×10^{-4}
$C_6H_5CH(OH)CH(CH_3)C_6H_5$	28795-94-0	30	1.5×10^{-5}
	28795-95-1	1	4.7×10^{-5}
		20	No reaction

TABLE II

PRODUCT DISTRIBUTION ON THE OXIDATION OF *meso*-HYDROBENZOIN AND *meso*-1,2-DIPHENYL-1,2-DIDEUTERIOETHANE-1,2-DIOL WITH NICKEL PEROXIDE[a]

Compd	Temp, °C	Products, % yield: Benzaldehyde	Products, % yield: Benzil
$(C_6H_5C(OH)H-)_2$	30	84.4	8.1
	1	71.2	31.8
	−11[b]	21.9	53.1
$(C_6H_5C(OH)D-)_2$	30	100	0
	−11[b]	45.3	Trace

[a] In benzene. [b] Unchanged 1,2-glycols were recovered.

For comparison of this reaction with a typical radical reaction of 1,2-glycols, azoisobutyronitrile was allowed to react with *meso*-hydrobenzoin to give benzil exclusively. Furthermore, investigation of the product distribution in the oxidation of *meso*-hydrobenzoin and *meso*-1,2-diphenyl-1,2-dideuterioethane-1,2-diol with nickel peroxide in order to reveal the difference between the radical oxidation and the oxidative cleavage with nickel peroxide was carried out to obtain the results as listed in Table II. Benzil did not react at all with nickel peroxide at 30°. This means that benzaldehyde is not afforded from benzil with nickel peroxide. The fact[3] that benzoin reacts with nickel peroxide to give a 98% yield of benzil suggests that the production of benzil from *meso*-hydrobenzoin with nickel peroxide would be attributable to the abstraction of α hydrogen of the glycol, which is the ordinary radical oxidation type, to yield benzoin followed by the oxidation of it. The substitution of deuterium for α hydrogen would make slowly the abstraction reaction at the α position to yield benzil.

For clarification of the characteristic of the reaction of 1,2-glycols with nickel peroxide, the relative oxidation rates of *meso*-hydrobenzoin, benzhydrol, and benzylphenylcarbinol are shown in Table I. The results suggest that substitution of the α-hydroxybenzyl group for the benzyl group increases the reactivity to nickel peroxide by about 800 times.

Subsequently, it could be assumed that the oxidative cleavage of 1,2-glycols with nickel peroxide takes place by way of a cyclic complex in a similar manner to that with lead tetraacetate and periodic acid.[6] However, if this were the case, a sharp distinction between the cis and trans glycols would be expected. Table III, where the reaction rates of the oxidation of *cis*- and *trans*-cyclopentane-1,2-diol with nickel peroxide are compared, shows that the behavior of 1,2-glycols with nickel peroxide, which is a one-electron oxidant type, is remarkably different from that with lead tetraacetate, the valence of which is immediately reduced

---

[1] Author to whom correspondence should be addressed.

[2] K. Nakagawa, K. Igano, and J. Sugita, *Chem. Pharm. Bull.*, **12**, 403 (1964).

[3] K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).

[4] R. Konaka, S. Terabe, and K. Kuruma, *ibid.*, **34**, 1334 (1969).

[5] I. Takashima, K. Yoneyama, and K. Watanabe, *Kogyo Kagaku Zasshi*, **69**, 1672 (1966).

[6] C. A. Bunton in "Oxidation in Organic Chemistry," part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 6.

TABLE III

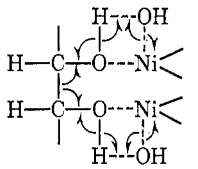
COMPARISON OF THE REACTION RATE OF THE OXIDATION OF *cis*- AND *trans*-CYCLOPENTANE-1,2-DIOL

Cyclopentane-1,2-diol	Rate ratio: Nickel peroxide k (sec^{-1}), 1°	Rate ratio: Lead tetraacetate[a] k (mol^{-1} l. min^{-1}), 20°
cis-	3.56×10^{-3}	40,000
trans-	1.69×10^{-3}	12.8
k_{cis}/k_{trans}	2.1	3,120

[a] R. Criegee, E. Büchner, and W. Walther, *Chem. Ber.*, **73**, 571 (1940).

by two units as pointed out by Heidt, Gladding, and Purves.[7]

Therefore, it is not unreasonable to propose that the oxidative cleavage of 1,2-glycols takes place by a concerted mechanism through the formation of a noncyclic nickel complex as shown tentatively below.



The result that the reaction rate of 1,2-diphenylpropyl alcohol with nickel peroxide was slow compared with *meso*-hydrobenzoin (Table I) suggests that the stepwise or concerted cleavage mechanism started from only one reaction site would not be probable, since the methyl group may stabilize the cleaved radical in a similar manner as the hydroxyl group.[8] Furthermore, the reaction of decahydronaphthalene-*trans*-9,10-diol with nickel peroxide did not occur at all at 20°, while that of the cis isomer proceeded even at 1° though it was not fast compared with *cis*- and *trans*-cyclopentane-1,2-diol (Table I and III). This means that both hydroxyl groups of decahydronaphthalene-*trans*-9,10-diol cannot simultaneously be bonded to the nickel peroxide surface.[8]

We conclude that in the oxidation reaction of 1,2-glycols with nickel peroxide two types of reaction occur competitively; the first type is an ordinary radical reaction beginning with α-hydrogen abstraction to produce diones, and the second is a concerted noncyclic mechanism on the two reaction site to yield C–C bond cleavage products.

Experimental Section

Materials.—*meso*-Hydrobenzoin and benzylphenylcarbinol were prepared from benzil and desoxybenzoin respectively by reduction with lithium aluminum hydride, and *meso*-1,2-diphenyl-1,2-dideuterioethane-1,2-diol and *meso*-2,3-dideuteriobutane-2,3-diol from benzil and biacetyl respectively with lithium aluminum deuteride, essentially according to the literature. Both deuterized compounds were confirmed by infrared spectrometry. Decahydronaphthalene-*cis*-9,10-diol was prepared from 1,2,3,4,5,6,7,8-octahydronaphthalene with osmium tetroxide, and the trans isomer by the oxidation of the octahydronaphthalene with *m*-chloroperbenzoic acid in a similar method of Shani and Sondheimer[9] followed by the treatment with acetic acid.[10] 1,2-Diphenylpropyl alcohol was synthesized from desoxybenzoin with methyl iodide and sodium ethoxide followed by the reduction with sodium borohydride. *cis*-Cyclopentane-1,2-diol was prepared by the oxidation of cyclopentene obtained from cyclopentanol and phosphoric acid, with potassium permanganate.[11] *trans*-Cyclopentane-1,2-diol was prepared by the oxidation of cyclopentene with hydrogen peroxide and formic acid.[12] Nickel peroxide was prepared by the method of Nakagawa, Konaka, and Nakata,[3] and its available oxygen content was 0.318×10^{-2} g-atom/g. *meso*-Butane-2,3-diol was commercially available.

Oxidation of *meso*-Hydro- and *meso*-Deuteriobenzoin with Nickel Peroxide.—A mixture of 0.032 mmol of *meso*-hydrobenzoin and 10 equiv of nickel peroxide was stirred vigorously by a magnetic stirrer in 34 ml of ether for 15 min at 30, 1, and −11°. After filtering off the nickel compound, the reaction mixture was analyzed by glpc (Schimazu GC-1B) to determine the yield of benzaldehyde and benzil (benzaldehyde, 30% silicone DC 550 column, 150° column temperature, ethylbenzene internal standard; benzil, 5% SE-30 column, 200° column temperature, benzophenone internal standard). *meso*-1,2-Diphenyl-1,2-dideuterioethane-1,2-diol was oxidized under the exactly same conditions and analyzed in the same way as described above. Benzaldehyde isolated from the reaction mixture in this oxidation reaction was confirmed to be C_6H_5CDO by infrared spectrometry.

Reaction of *meso*-Hydrobenzoin with Azoisobutyronitrile.—A solution of 0.6 mmol of *meso*-hydrobenzoin and 0.9 mmol of azoisobutyronitrile in 20 ml of benzene was heated at 65–70° for 1 hr under the nitrogen atmosphere. The reaction mixture was analyzed by the glpc method, used in the case of the oxidation with nickel peroxide, to determine a 21.4% yield of benzil, a 76.1% recovery of *meso*-hydrobenzoin, and no benzaldehyde.

Oxidation Rate of 1,2-Glycols and Related Compounds with Nickel Peroxide.—Two techniques were applied depending on the order of the reaction rate involved. The oxidation reaction rates of *meso*-hydrobenzoin and *meso*-1,2-diphenyl-1,2-dideuterioethane-1,2-diol, which are too fast to follow by the glpc method, were measured by the thermoanalytical technique developed by Takashima, Yoneyama, and Watanabe,[5] in which the change of reaction heats was followed on stirring a solution of 3 mmol of the substrate and 5 equiv of nickel peroxide in 150 ml of benzene with vigorous and constant rotation at 31°.

The reaction rates of *meso*-butane-2,3-diol, *meso*-2,3-dideuteriobutane-2,3-diol, benzylphenylcarbinol, and *cis*- and *trans*-cyclopentane-1,2-diol were measured by following the diol or the alcohol in the reaction mixture which resulted from oxidation of the substrate with 5 equiv of nickel peroxide in ether, using glpc for analysis [column, 5% PEG (*meso*-butane-2,3-diol, *cis*- and *trans*-cyclopentane-1,2-diol), Carbowax (benzylphenylcarbinol), 5% DEGS (benzhydrol, decahydronaphthalene-*cis*-9,10-diol, 1,2-diphenylpropyl alcohol); internal standard, naphthalene (*meso*-butane-2,3-diol), azobenzene (benzylphenylcarbinol, benzhydrol), acenaphthene (*cis*- and *trans*-cyclopentane-1,2-diol), benzophenone (decahydronaphthalene-*cis*-9,10-diol), benzil (1,2-diphenylpropyl alcohol)].

All oxidation reaction rates were expressed by the pseudo-first-order reaction rate equation. The measurements of the reaction rates were repeated two or three times. For example, we obtained 3.5 and 4.1×10^{-2} sec^{-1} in the oxidation of *meso*-hydrobenzoin, and 6.2, 5.6, and 4.2×10^{-4} sec^{-1} in the case of benzhydrol. In addition, the Arrhenius plots in the oxidation of *meso*-hydrobenzoin showed a straight line to give the activation energy of 5.69 kcal/mol, though it was derived from only three temperatures over a range of only 20°.

It was found that mainly acetaldehyde was produced on the oxidation of *meso*-butane-2,3-diol with nickel peroxide, but biacetyl, which is not converted to acetaldehyde by nickel peroxide, was not produced. The oxidation products of benzylphenylcarbinol were acetaldehyde and benzil. The initial major oxidation product from *cis*- and *trans*-cyclopentane-1,2-diol with nickel peroxide was glutaraldehyde, confirmed as the 2,4-dinitrophenylhydrazone.

Registry No.—Nickel peroxide, 1313-99-1; *cis*-cyclopentane-1,2-diol, 5057-98-7; *trans*-cyclopentane-1,2-diol, 5057-99-8.

---

(7) L. J. Heidt, E. K. Gladding, and C. B. Purves, *Paper Trade J.*, **121**, 35 (1945); *Chem. Abstr.*, **40**, 546 (1946).

(8) The authors wish to thank the referees for the suggestion concerning these experiments.

(9) A. Shani and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 6310 (1967).

(10) C. A. Grob and P. W. Shiess, *Helv. Chim. Acta*, **43**, 1546 (1960).

(11) P. D. Bartlett and A. Bavley, *J. Amer. Chem. Soc.*, **60**, 2416 (1938).

(12) A. Roebuck and H. Adkins, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 217.