alcohol was refluxed for 26 hours. The precipitated product was filtered and washed with ether; yield 0.36 g. (41%), m.p. 285–286° dec.

Anal. Calcd. for $C_{18}H_{36}N_2Cl_2$: N, 7.98; Cl^-, 20.18. Found: N, 7.94; Cl^-, 19.92.

N,N,N′,N′-Dioctamethylenepiperazinium Dichloride.—The base, obtained from 2.4 g. of the hydrochloride, was treated in the manner described above; yield 0.37 g. (20%), m.p. 275–276° dec.

Anal. Calcd. for $C_{20}H_{40}N_2Cl_2$: N, 7.38; Cl^-, 18.66. Found: N, 7.37; Cl^-, 18.62.

N,N,N′,N′-Di-(1-methylhexamethylene)-piperazinium Dichloride.—The base was isolated from 3.0 g. of the required hydrochloride, and treated as described above. The product weighed 1.2 g. (49%); m.p. 276–277° dec.

Anal. Calcd. for $C_{18}H_{36}N_2Cl_2$: N, 7.98; Cl^-, 20.18. Found: N, 7.93; Cl^-, 20.14.

Isomerization.—It was found that the hydrochlorides of the two isomeric compounds, 2-methyl-2-(1-hexamethylenimino)-ethyl chloride (14) and 1-methyl-2-(1-hexamethylenimino)-ethyl chloride (9), melted at the same temperature (m.p. 198–199°, mixed m.p. 198–199°). When each of these hydrochlorides was converted into a picrate, one picrate (14′) melted at 117–118°, the other (9′) at 127–128°. We believe that during the melting point determination, the one hydrochloride (14) was converted into the isomeric hydrochloride (9).

2-Methyl-2-(1-hexamethylenimino)-ethyl chloride picrate, m.p. 117–118°, was heated at 130° for 4 minutes. The material was then crystallized from methyl ethyl ketone-heptane, and it proved to be 1-methyl-2-(1-hexamethylenimino)-ethyl chloride picrate; mixed m.p. 127–128°.

Four other compounds (Table VII, 15, 16, 17 and 18) behaved in a similar manner and yielded the four isomers (Tables VII, 1, 11, 12 and 13).

Cpd. 15 (m.p. 89–90°) $\xrightarrow{105°}$ cpd. 10 (mixed m.p. 102–103°)

Cpd. 16 (m.p. 158–159°) $\xrightarrow{162-165°}$ cpd. 11 (mixed m.p. 176–177°)

Cpd. 17 (m.p. 132–133°) $\xrightarrow{140°}$ cpd. 12 (mixed m.p. 158–159°)

Cpd. 18 (m.p. 115–117°) $\xrightarrow{125°}$ cpd. 13 (mixed m.p. 127–128°)

The free bases of 14, 16, 17 and 18 (Table VII) did not isomerize, in ether solution, during a two-hour period at room temperature.

During distillation, the base of 17 isomerized to the base of 12.

Ann Arbor, Michigan

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Organic Peroxides. XIX. α-Hydroperoxyethers and Related Peroxides

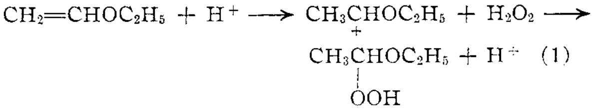
By Nicholas A. Milas, Robert L. Peeler, Jr.,[1] and Orville L. Mageli

Received November 3, 1953

Several α-hydroperoxyethers have been synthesized by the controlled addition of hydrogen peroxide to the corresponding vinyl ethers. Some of the reactions of these hydroperoxides which have a bearing on their structure have been studied and elucidated. Some of these reactions include spontaneous or thermal decomposition or decomposition in the presence of ferrous ions.

It has been known for some time[2-4] that ethers form peroxides when exposed to air or oxygen. Although the initial peroxides are assumed to be α-hydroperoxyethers very few instances are known in which peroxides of this structure have been isolated in the pure state. With the single exception of 2-hydroperoxytetrahydrofuran[5,6] the peroxides isolated are secondary products which belong to the highly explosive alkylidene peroxide group.[7] For example, from ethyl and diisopropyl ethers only the polymeric ethylidene peroxide[4] and the trimeric isopropylidene (acetone) peroxide[8,9] were isolated, respectively.

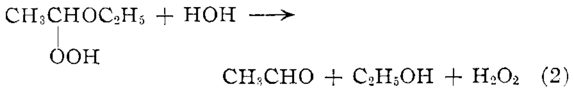
Rieche and Meister[4] attempted the synthesis of α-hydroperoxyethyl ether by the dehydration of a mixture of α-hydroxyethyl hydroperoxide and ethanol with phosphorus pentoxide but they obtained a highly explosive viscous oil which behaved more like ethylidene peroxide than α-hydroperoxyethyl ether. We now wish to report a successful synthesis of this and other α-hydroperoxyethers by the modification of a method originally published from this Laboratory.[10] α-Hydroperoxyethyl ether was synthesized by allowing hydrogen peroxide to add to ethyl vinyl ether in the presence of a trace of sulfuric acid as a catalyst.



$$CH_2{=}CHOC_2H_5 + H^+ \longrightarrow CH_3\underset{+}{C}HOC_2H_5 + H_2O_2 \longrightarrow CH_3\underset{\substack{|\\ OOH}}{C}HOC_2H_5 + H^+ \quad (1)$$

I

This peroxide was easily purified by distillation and was found to have the correct analysis for the formula assigned to it. Furthermore, a Zerewitinoff determination indicated the presence of one active hydrogen and an infrared spectrum showed a prominent band at 11.92 μ due to the hydroperoxy group, a broadened band at 3 μ due to the hydroxyl group of the hydroperoxy radical and a strong ether band at 9 μ. Upon heating with water, it decomposed quantitatively in accordance with equation 2. When treated with ferrous ions at 0 to 5° it gave mainly ethyl acetate. This reaction



$$CH_3\underset{\substack{|\\ OOH}}{C}HOC_2H_5 + HOH \longrightarrow CH_3CHO + C_2H_5OH + H_2O_2 \quad (2)$$

---

[1] M.S. Thesis, M.I.T., 1949.

[2] A. M. Clover, This Journal, **44**, 1107 (1922).

[3] N. A. Milas, *ibid.*, **53**, 221 (1931).

[4] A. Rieche and R. Meister, *Angew. Chem.*, **49**, 101 (1936).

[5] A. Robertson, *Nature*, **162**, 153 (1948).

[6] H. Rein and R. Criegee, *Angew. Chem.*, **62**, 120 (1950).

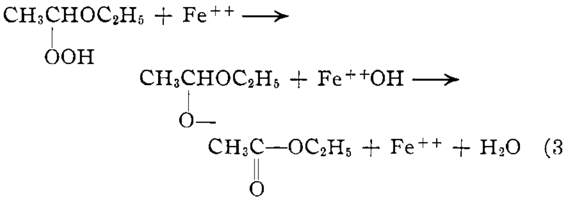
[7] N. A. Milas, *Ency. Chem. Technology*, **10**, 70 (1953).

[8] A. Rieche and K. Koch, *Ber.*, **75**, 1016 (1942).

[9] F. Acree and H. L. Haller, This Journal, **65**, 1652 (1943).

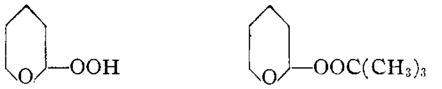
[10] N. A. Milas, U. S. Patent 2,223,807 (Dec. 3, 1940).

may be explained as an electron transfer reaction in which the intermediate product is a free radical[11,12]



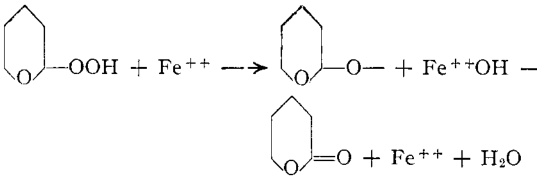
$$\underset{\text{OOH}}{\text{CH}_3\text{CHOC}_2\text{H}_5} + \text{Fe}^{++} \longrightarrow \underset{\text{O—}}{\text{CH}_3\text{CHOC}_2\text{H}_5} + \text{Fe}^{++}\text{OH} \longrightarrow \underset{\text{O}}{\overset{}{\text{CH}_3\text{C}}}\text{—OC}_2\text{H}_5 + \text{Fe}^{++} + \text{H}_2\text{O} \quad (3)$$

2-Hydroperoxytetrahydropyran (II) and *t*-butyl-2-tetrahydropyran peroxide (III) were also synthesized by the addition of hydrogen peroxide and *t*-butylhydroperoxide, respectively, to 2,3-dihydro-1,4-pyran in the presence of traces of sulfuric acid.



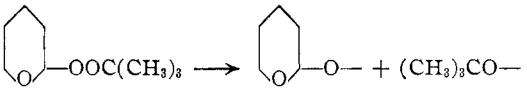
II III

On standing at room temperature 2-hydroperoxytetrahydropyran decomposes slowly into 2-hydroxytetrahydropyran while at higher temperatures it gives mainly δ-valerolactone. When the decomposition of this peroxide is catalyzed by ferrous ions, the main product formed is δ-valerolactone.



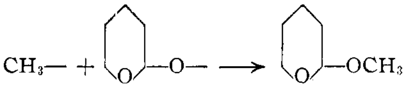
(4)

When *t*-butyl-2-tetrahydropyran peroxide was thermally decomposed at 250° in a tube packed with glass wool[13] the products isolated were acetone, 2-methoxytetrahydropyran, δ-valerolactone, di-2-tetrahydropyran ether and a non-condensable hydrocarbon gas which was probably ethane. Di-2-tetrahydropyran ether is known to form by the dehydration of 2-hydroxytetrahydropyran. The formation of these products is best accounted for on the basis of the free radical mechanism as shown in equations 5–8.

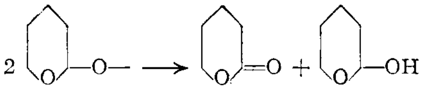


(5)

$$(\text{CH}_3)_3\text{CO—} \longrightarrow (\text{CH}_3)_2\text{CO} + \text{CH}_3\text{—} \quad (6)$$



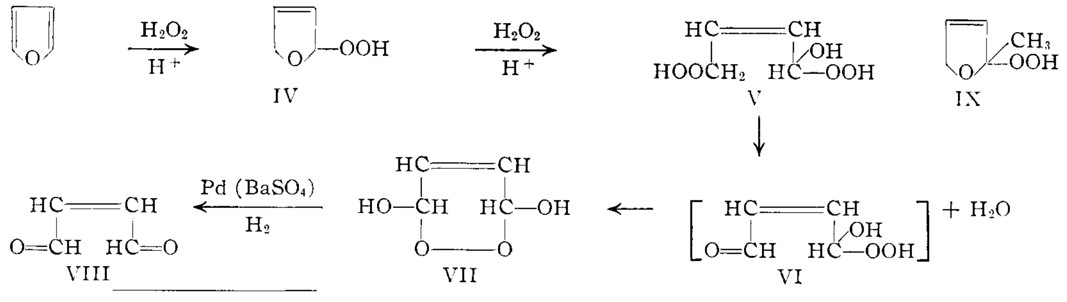
(7)



(8)

The addition of hydrogen peroxide to furan and 2-methylfuran also was investigated. With furan an unstable peroxide was isolated which showed the presence of two hydroperoxy groups but qualitative tests indicated the presence of free hydrogen peroxide. When this was removed by repeated extractions with a saturated solution of ammonium sulfate another peroxide was isolated which analyzed for one active oxygen per mole and which yielded malealdehyde on catalytic hydrogenation. On standing at room temperature both peroxides were slowly converted into maleic acid, the one with the higher active oxygen content yielded larger amounts. These reactions may be best interpreted by the stepwise addition of hydrogen peroxide to furan to form first the monohydroperoxide IV which was not isolated since it was rapidly converted to the dihydroperoxide V. Since primary hydroperoxides are less stable than hydroxyhydroperoxides,[7] the primary hydroperoxy group would lose water to yield the intermediate VI which is expected to go over to a more stable form VII. On catalytic hydrogenation this is converted to malealdehyde (VIII) isolated as its 2,4-dinitrophenylhydrazone.

With 2-methylfuran the hydroperoxide IX was definitely isolated as an amorphous powder. It is unsaturated since it absorbs 2.2 moles of hydrogen. A Zerewitinoff determination showed the presence of one active hydrogen. An infrared absorption spectrum showed two bands characteristic of the hydroperoxy group: one at 2.8–3.1 μ due to the hydrogen stretching vibration of the hydroperoxy group[14] and another at 11.8–12 μ due to the hydroperoxy group itself.[15] The latter band may not be significant in this case since 2-methyltetrahydrofuran shows a broad band in this region.[16] An attempt to study the decomposition of this peroxide and the further addition of hydrogen peroxide to it produced unsaturated keto aldehydes and polymeric products which were difficult to identify.



IV V IX VI VII VIII (9)

Experimental Part

α-Hydroperoxyethyl Ether.—Into a cold (0°) mixture of hydrogen peroxide (100 g. of 48%) and sulfuric acid (0.37 g. of 95.5%) in an open beaker equipped with a stirrer, thermometer and a dropping funnel was added dropwise in

---

[11] R. J. Orr and H. L. Williams, *Can. J. Chem.*, **30**, 985 (1952).

[12] W. S. Wise and G. H. Twigg, *J. Chem. Soc.*, 2172 (1953).

[13] N. A. Milas and D. M. Surgenor, This Journal, **63**, 205 (1946).

[14] R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

[15] N. A. Milas and O. L. Mageli, This Journal, **75**, 5970 (1953).

[16] G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

the course of 2.5 hours 72 g. (1.0 mole) of ethyl vinyl ether,[17] b.p. 37°. Stirring was continued for an additional hour, then an excess of saturated ammonium sulfate solution was added in order to remove the unused hydrogen peroxide and to moderate the reaction. The mixture was then extracted with ethyl ether and the extract washed with a saturated solution of sodium bicarbonate then with water and dried over magnesium sulfate at −9°. The ether solution, after separation from the drying agent, was distilled at 2 mm. from a water-bath maintained at 40–45° and the distillate collected in traps kept at 0° and at −70°. The distillate (24.8 g.) collected at 0° had the following properties: it is a neutral, colorless liquid with a characteristic organic peroxide odor; $n^{25}\text{D}$ 1.4091, $d^{25}{}_4$ 1.005, MR_D (calcd.)[18] 26.09, MR_D (obsd.) 26.09.

Anal. Calcd. for $C_4H_{10}O_3$: C, 45.27; H, 9.50; (O), 15.1; (Zerewitinoff H), 1.00. Found: C, 45.85; H, 9.65; (O), 15.56; (Zerewitinoff H), 1.03.

When an aqueous solution of this peroxide was heated with an excess reagent of 2,4-dinitrophenylhydrazine in aqueous alcoholic solution, a quantitative yield, based on equation 2, of 2,4-dinitrophenylhydrazone of acetaldehyde, m.p. 157°, was obtained.

Decomposition by Fe^{++}.—To 20 g. of ferrous sulfate dissolved in 100 cc. of water and maintained at 0 to 5° was added, dropwise in the course of one hour and with occasional shaking, 10 g. of α-hydroperoxyethyl ether in 30 cc. of water. The mixture was then subjected to distillation and from the distillate was obtained an organic layer which was redistilled and the fraction (4.7 cc.) boiling at 76–77° collected: $n^{25}\text{D}$ 1.3690. This was identified as ethyl acetate.

2-Hydroperoxytetrahydropyran (II).—To a cold (0°) mixture of 34 g. (0.5 mole) of 50% hydrogen peroxide and 0.1 cc. of 95.5% sulfuric acid in an open beaker was added, with stirring in the course of 20 minutes, 21 g. (0.25 mole) of 2,3-dihydro-1,4-pyran,[19] b.p. 83–84°. The temperature of the mixture was not allowed to rise above 10° during the reaction. Stirring was continued for an additional hour, then the mixture was saturated with solid ammonium sulfate and extracted with ethyl ether. The ether extract was repeatedly shaken with a saturated solution of ammonium sulfate until it failed to give a positive test with silver foil for free hydrogen peroxide. Finally, it was dried over magnesium sulfate, filtered and the ether removed under reduced pressure at room temperature. The residue was then fractionated under reduced pressure, using a hot water-bath at 75°, from a Claisen flask to which was sealed a 6″ column packed with glass rings and the fraction (16.6 g.) boiling at 58–59° (3 mm.) collected and analyzed. A non-volatile peroxidic residue (6–7 g.) probably consisting of di-2-tetrahydropyran peroxide and other products remained in the flask. The distillate was a colorless, viscous liquid; $n^{25}\text{D}$ 1.1136, MR_D (calcd.)[18] 28.45, MR_D (obsd.) 28.42.

Anal. Calcd. for $C_5H_{10}O_3$: C, 50.83; H, 8.53; (O), 13.54. Found: C, 50.67; H, 8.55; (O), 13.56.

Although this peroxide is fairly stable at 0° for long periods of time it decomposes slowly at room temperature to give mainly 2-hydroxytetrahydropyran. For example, a sample (15 g.) was allowed to decompose at room temperature for 35 days. At the end of this period more than 90% of the peroxide activity was lost. The sample was distilled under reduced pressure and the fraction (8.1 g.) boiling at 78–80° (3–4 mm.) was collected and analyzed; $n^{25}\text{D}$ 1.4550, $d^{25}{}_4$ 1.099.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.80; H, 9.86. Found: C, 58.95; H, 8.06.

The low value for the hydrogen analysis of the 2-hydroxytetrahydropyran may be attributed to the presence of δ-valerolactone which was difficult to remove without appreciable decomposition of the main product. When a portion of the above distillate was heated with 2,4-dinitrophenylhydrazine in dilute sulfuric acid, the 2,4-dinitrophenylhydrazone of δ-hydroxyvaleraldehyde was formed in appreciable quantities. This was recrystallized from ethanol, m.p. 69–70°.

Anal. Calcd. for $C_{11}H_{14}O_5N_4$: C, 46.80; H, 5.01. Found: C, 46.12; H, 5.32.

When a sample (5 g.) of 2-hydroperoxytetrahydropyran was heated in a Claisen flask at 98–99° for six hours, the peroxide decomposed completely into a yellowish viscous liquid which was subjected to vacuum distillation and the distillate boiling at 56–59° (3 mm.) collected and allowed to stand at room temperature for several days; it solidified into a white waxy solid, m.p. 44–46°. Fichter and Beisswenger[20] reported a m.p. of 47–48° for the polymer of δ-valerolactone.

Decomposition by Fe^{++}.—To 5.0 g. of 2-hydroperoxytetrahydropyran dissolved in 50 cc. of water was added 15 g. of ferrous sulfate heptahydrate. Heat was evolved and there was an immediate precipitate of ferric hydroxide. The mixture was heated at 75° for one-half hour, cooled and extracted with ether. The ether extract was dried and the ether removed in vacuum. The residue was distilled under reduced pressure and the fraction boiling at 70–75° (2–3 mm.) collected and analyzed; $n^{25}\text{D}$ 1.4358, $d^{25}{}_4$ 1.004.

Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.06. Found: C, 59.73; H, 8.91.

This product was not completely soluble in 10% aqueous sodium hydroxide and gave a positive aldehyde test with fuchsine reagent showing that it contained small amounts of 2-hydroxytetrahydropyran.

***t*-Butyl-2-tetrahydropyran Peroxide.**—To a mixture of 37.5 g. (0.25 mole) of 60% *t*-butylhydroperoxide (Lucidol) and 1 cc. of 6 *N* sulfuric acid in a 150 cc. beaker immersed in an ice-bath was added dropwise, in the course of 20 minutes with rapid stirring, 21 g. of 2,3-dihydro-1,4-pyran. Stirring was continued at 0° for six hours longer, then 50 cc. of ethyl ether was added and the mixture extracted with 50 cc. of 10% sodium hydroxide solution. The ethereal solution was then dried and the ether and other volatile materials removed at 20 mm. pressure. The residue was fractionated at 2 mm. and the fraction boiling at 40–41° collected and analyzed; yield 60–70%, $n^{25}\text{D}$ 1.4355, $d^{25}{}_4$ 0.956; MR_D (calcd.) 47.04, MR_D (obsd.) 47.62.

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.08; H, 10.41; (O), 9.18. Found: C, 61.90; H, 9.62; (O), 9.14.

Thermal Decomposition of *t*-Butyl-2-tetrahydropyran Peroxide.—The apparatus used for the thermal decomposition of this peroxide was essentially the same as that described elsewhere.[13] It consisted of a 16-mm. Pyrex tube packed loosely with glass wool and heated electrically in a vertical furnace at a temperature of 245–255°. The condensable decomposition products were caught in three traps connected in series and cooled in solid carbon dioxide–acetone baths. The non-condensable vapors were collected over water.

After the system had been flushed out with dry nitrogen, 20 g. of *t*-butyl-2-tetrahydropyran peroxide was dropped slowly into the hot tube in the course of 1.25 hours. A colorless liquid (14.2 g.) was collected in the traps and 2030 cc. of gas at 27.5° was collected over water. The liquid was fractionally distilled and the fractions together with their physical properties are shown in Table I.

TABLE I

FRACTIONATION OF LIQUID PRODUCTS FROM THE THERMAL DECOMPOSITION OF *t*-BUTYL-2-TETRAHYDROPYRAN PEROXIDE

Fraction	Wt., g.	B.p., °C.	*P*, mm.	$n^{25}\text{D}$	$d^{25}{}_4$
1	5.5	54–56	767	1.3599	0.789
2	2.4	45–48	15	1.3966	.891
3	0.5	48–65	2.5	1.4261	.923
4	2.2	70–79	2.5	1.4360	.995

Fraction 1 was identified as acetone; 2,4-dinitrophenylhydrazone, m.p. 123–124°. Fraction 2 was identified as 2-methoxytetrahydropyran; MR_D (calcd.) 30.99, MR_D (obsd.) 31.13.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.03; H, 10.41. Found: C, 62.34; H, 9.45.

When this ether was hydrolyzed with 6 *N* sulfuric acid, 2-hydroxytetrahydropyran was formed which gave a positive aldehyde test with fuchsine and a 2,4-dinitrophenylhydra-

---

(17) Purified from the commercial product supplied to us by General Aniline and Film Corporation.

(18) N. A. Milas, D. M. Surgenor and L. H. Perry, THIS JOURNAL, **68**, 1617 (1946).

(19) Purified from a commercial product supplied to us by E. I. du Pont and Co.

(20) Fr. Fichter and A. Beisswenger, *Ber.*, **36**, 1200 (1903).

zone identical with that formed from an authentic sample of 2-hydroxytetrahydropyran.

Fraction 3 was not definitely identified although it was partly soluble in alkali and must have contained some δ-valerolactone. The properties of fraction 4 indicated that it was a mixture of δ-valerolactone and a product insoluble in 10% alkali. Since this fraction failed to give an aldehyde test, the product insoluble in alkali cannot be 2-hydroxytetrahydropyran which is known[21] to lose readily a molecule of water at high temperatures and to go over to di-2-tetrahydropyran ether. In fact, a carbon and hydrogen analysis of this fraction gave values corresponding to about equal quantities of δ-valerolactone and di-2-tetrahydropyran ether.

1-Hydroxy-1,4-dihydroperoxybutene (V).—To a cold (0°) mixture of sulfuric acid (30 g. of 95.5%) and hydrogen peroxide (70 g. of 48%) was added, dropwise with stirring in the course of one hour, 34 g. (0.5 mole) of furan.[19] The temperature was maintained at 0 ± 5°. Stirring was continued for 1.5 hours longer at 0°, then the mixture was saturated with solid ammonium sulfate and extracted with ethyl ether. The ether extract was shaken once with magnesium carbonate, dried at −9° and the ether removed under reduced pressure. The yellow residual oil was subjected to distillation at 2 mm. and at water-bath temperature of 40°; a small amount (*ca.* 1 g.) of a yellow oil distilled over which gave the following analyses.

Anal. Calcd. for $C_4H_8O_5$ (V): C, 35.30; H, 5.92; (O), 23.6. Found: C, 36.85; H, 4.42; (O), 20.8.

This peroxide decomposes readily to maleic acid which was identified by m.p. and mixed m.p. with an authentic sample. The presence of this acid in the analytical sample would tend to raise the carbon and lower the hydrogen and active oxygen content and therefore account for the results obtained. The yellow oil also gave a positive test with a silver foil for the presence of hydrogen peroxide.

1,4-Dihydroxy-1,4-exocycloperoxene-2 (VII).—When a large sample of the crude peroxide V was repeatedly extracted with a saturated solution of ammonium sulfate another peroxide was formed and isolated as a yellow oil which failed to give a positive test for hydrogen peroxide; n^{25}_D 1.4947.

Anal. Calcd. for $C_4H_6O_4$: C, 40.68; H, 5.12; (O), 13.6. Found: C, 39.00; H, 4.98; (O), 15.7.

On standing at room temperature this peroxide was also converted, in part, into maleic acid and a yellow polymer. When it was reduced in ethanol with hydrogen, using palladium catalyst (2%) deposited on barium sulfate, malealdehyde was isolated and converted into its bis-phenylhydrazone according to a recent method[22]; m.p. 184–186° (lit. 180–184°).

Anal. Calcd. for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.92; H, 6.15; N, 20.93.

2-Methyl-2-hydroperoxy-2,5-dihydrofuran (IX).—Into a cold (0°) mixture of hydrogen peroxide (19.5 g. of 48%) and sulfuric acid (17.3 g. of 95.5%) was added, dropwise with stirring in the course of one hour, 20.5 g. (0.25 mole) of methylfuran.[19] The temperature of the reaction was maintained at 0 ± 5°. A red color developed during the addition of methylfuran and the mixture became thick and sticky and difficult to stir efficiently. It was found essential to add 50 cc. of anhydrous ether to dissolve the sticky material and facilitate stirring. The mixture was stirred for an additional hour, then the non-aqueous layer separated, extracted with saturated ammonium sulfate solution, then shaken with magnesium carbonate and dried. When the ether was removed under reduced pressure a yellowish, peroxidic oil (9 g., 34% of theory) was obtained. This had an active oxygen content of 9.9% as against the theoretical of 13.8%. This preparation was repeated using anhydrous ether as a solvent from the beginning of the reaction. In this case a crude product was obtained in 70% yield with an active oxygen content of 11.2%.

This hydroperoxide cannot be crystallized but can be obtained as a white powder from ethyl ether by the addition of small quantities of petroleum ether. When well dried, it explodes upon heating and decomposes without melting at 80–100°.

Anal. Calcd. for $C_5H_8O_3$: C, 51.77; H, 6.95; (O), 13.8; (Zerewitinoff H), 1.0. Found: C, 50.66; H, 6.83; (O), 13.2; (Zerewitinoff H), 1.1.

When catalytically hydrogenated in ethanol, using platinum oxide as catalyst, it absorbed 1.1 moles of hydrogen, while in glacial acetic acid, it absorbed 2.2 moles of hydrogen. It also absorbed bromine slowly in ethyl acetate showing definitely that it was unsaturated. An infrared spectrum showed three bands at 2.8–3.1 μ, 9 μ and 11.8–12 μ characteristic, respectively, of the hydroxyl radical of the hydroperoxy group, the ether linkage and the hydroperoxy radical. Molecular weight determinations in dioxane by the cryoscopic method[23] failed to give reproducible results showing that this hydroperoxide may be polymeric or polymerizes in dioxane.

Acknowledgment.—We are indebted to Lucidol Division of Novadel-Agene Corporation and E. I. du Pont de Nemours and Co. for financial support of this investigation. For the combustion analyses and the infrared spectra we wish to thank Dr. Nagy and his associates of this Institute.

CAMBRIDGE, MASS.

---

(21) R. Paul, *Bull. soc. chim.*, [5] **1**, 971 (1934).

(22) N. Clauson-Kaas, F. Limborg and K. Glens, *Acta Chem. Scand.*, **6**, 531 (1952).

(23) O. L. Mageli, Ph.D. Thesis, M.I.T., April, 1953, p. 16.

[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE ORTHO RESEARCH FOUNDATION]

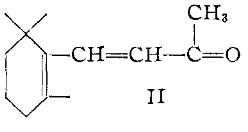
Synthesis of Polyenes. IV. The Reaction of β-Ionone with Grignard Reagents

BY WILLIAM OROSHNIK, GEORGE KARMAS AND ROBERT A. MALLORY

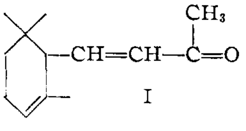
RECEIVED DECEMBER 9, 1953

Contrary to general belief, β-ionone has been found to react normally with Grignard reagents to give the 1,2-adduct as major product and the 1,4-adduct in minor amount. Evidence is presented correlating the predominance of the 1,2-addition with the steric hindrance in β-ionone. The spectral characteristics of the resulting β-ionols are discussed.

For quite some time now, β-ionone (I) has been assumed to react abnormally with ordinary Grignard reagents. This concept stems from the original report on this reaction by Karrer, *et al.*,[1] who could obtain no carbinol from β-ionone with allylmagnesium bromide in spite of the fact that α-ionone (II) gave the expected 1,2-adduct with this reagent. To account for these results it was suggested that a 1,4-adduct was formed with β-ionone, but no details of the characteristics of the product were given.[1] Since then similar failures to achieve



II



I

---

(1) P. Karrer, H. Salomon, R. Morf and O. Walker, *Helv. Chim. Acta*, **15**, 878 (1932).