Studies in Organic Peroxides. XXX. Organic Peroxides Derived from 2,5-Hexanedione and Hydrogen Peroxide[1a]

NICHOLAS A. MILAS AND ALEKSANDAR GOLUBOVIC[1b]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Massachusetts

Received June 21, 1962

The reaction of 2,5-hexanedione with hydrogen peroxide in the absence of mineral acids led to the isolation and identification of two new organic cyclic peroxides. From their infrared and n.m.r. spectra and their instability to mineral acids, they were shown to be derivatives of tetrahydrofuran and tentatively have been assigned structures VI and VII. The reaction of 2,5-hexanedione with hydrogen peroxide in the presence of mineral acids takes a different course and the dihydroperoxy peroxide IV isolated was shown to have a six- instead of a five-membered ring structure. Both peroxides IV and VI form crystalline bis-*p*-nitrobenzoates which gave the correct analyses and other properties and can, therefore, be used for identification purposes.

In a previous publication[2] we have described the structure of the peroxides derived from the reaction of 2,4-pentanedione and hydrogen peroxide. The present communication will describe the structure of the peroxides derived from the reaction of 2,5-hexanedione (acetonylacetone) and hydrogen peroxide. The reaction of 2,5-hexanedione with hydrogen peroxide in acid solution has been reported in the patent literature[3] but only polymeric products of unknown constitution have been isolated.

We have found that when 2,5-hexanedione was allowed to react in the absence of acid with 50% hydrogen peroxide at room temperature for four days, a mixture of five different peroxides was formed as detected by paper chromatography.[4] Each peroxide present in the mixture was estimated by its R_f to be approximately as follows R_f: 0.00, about 85%; 0.09, traces; 0.220, 9%: 0.350, traces; 0.665, 6%. When the reaction mixture was extracted with pentane all peroxides, except the one with R_f, 0.00, went into the pentane layer. After washing with a saturated solution of ammonium sulfate and drying, the pentane solution was cooled to −70°. Although the crystals which separated contained mainly the peroxide with R_f 0.220, there were also traces of the peroxides with R_f 0.09 and 0.350, respectively. The crystals were finally subjected to cellulose powder chromatography using the technique previously reported[5] and the peroxide obtained had a m.p. of 135° and gave a single spot on a paper chromatogram with R_f 0.220. An infrared spectrum 10% in chloroform of this peroxide showed, in addition to hydrogen bonded —OH and —OOH, strong bands for —O—O— and —O— groups. Hydrogen bonding of the hydroperoxy groups has also been assigned to the n.m.r. band at 637 c.p.s. (Fig. 1) and the absence of vinylic hydrogen lends support to structure VI (Fig. 2). Moreover, analytical data including the molecular weight determined in dioxane by the cryoscopic method are in favor of this structure. Additional support was afforded by the preparation of its bis-*p*-nitrobenzoate derivative which gave the correct analysis and molecular weight, and its infrared spectrum showed a strong perester band at 1766-1760 cm.$^{-1}$ and two bands at 850 and 870 cm.$^{-1}$, respectively, due to —O—O— groups.

The pentane mother liquor, after all of peroxide VI had been removed at low temperatures, contained the peroxide with R_f 0.665 contaminated with traces of peroxides with R_f 0.09 and 0.350. The pentane solution therefore was subjected to column cellulose chromatography and the peroxide with R_f 0.665 obtained in the pure state. This peroxide is very volatile and reacts very slowly with potassium iodide in glacial acetic acid. Its infrared spectrum 10% in chloroform failed to show any —OH or —OOH bands but had strong bands in the regions attributed to —O—O— and —O— groups. From the analytical data and molecular weight determinations, it can best be represented by structure VII. An n.m.r. spectrum of this peroxide (Fig. 3a) shows the presence of only $—CH_2—$ and $—CH_3$ groups and excludes the presence of vinylic hydrogens, thereby strengthening the evidence for structure VII.

Both peroxides VI and VII are sensitive to acid hydrolysis. Parallel experiments were performed in which each peroxide, in water solution with and without a drop of sulfuric acid, was shaken for twenty-four hours at room temperature. The one with the acid was completely decomposed (loss of active oxygen), while the one without the acid showed no change in active oxygen. This is easily understandable since peroxides, like ozonides, which contain ether groups flanked by peroxy or hydroperoxy groups are sensitive to mineral acid hydrolysis.[2]

When the mole ratio of 2,5-hexanedione to hydrogen peroxides was 1:1, 1:2, or 1:3, the number of peroxides formed was essentially the same with the peroxide R_f 0.00 present in the largest amount, but when the ratio was changed to 1:4, the latter peroxide was the only peroxide formed. This peroxide is a highly viscous liquid with an active oxy-

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[1] (a) Originally submitted to *J. Am. Chem. Soc.*, February 2, 1961; (b) Lucidol Research Associate.

[2] N. A. Milas, A. Golubovic, O. L. Mageli, R. W. Arndt, and J. C. J. Ho, Paper XXIX, *J. Am. Chem. Soc.*, **85**, in press.

[3] H. Rudoff, U.S. Patent 2,424,851, July 29, 1947.

[4] N. A. Milas and I. Belič, *J. Am. Chem. Soc.*, **81**, 3358 (1959).

[5] N. A. Milas and A. Golubović, *ibid.*, **81**, 3361 (1959).

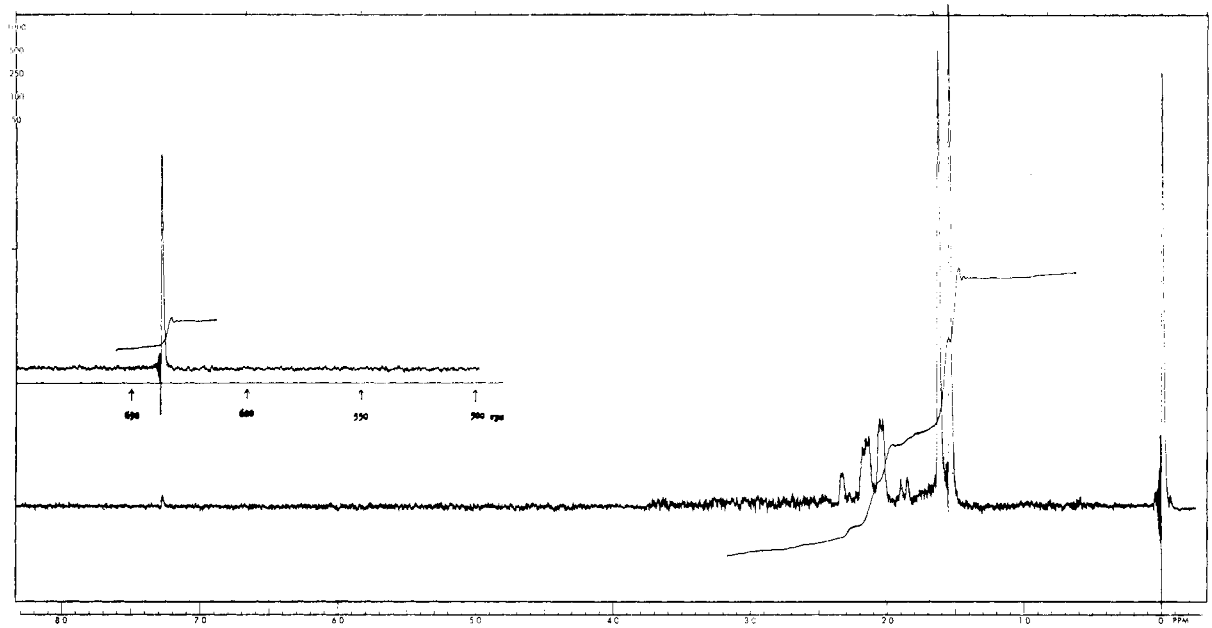

Fig. 1.—N.m.r. spectrum of peroxide VI 15% in deuteriochloroform taken at 60 Mc./sec. Chemical shifts are in p.p.m. referenced from tetramethylsilane as internal standard. The band at 637 c.p.s. of 10.61 p.p.m. is attributed to hydrogen bonding of the hydroperoxy groups with the oxygen of the substituted tetrahydrofuran ring.

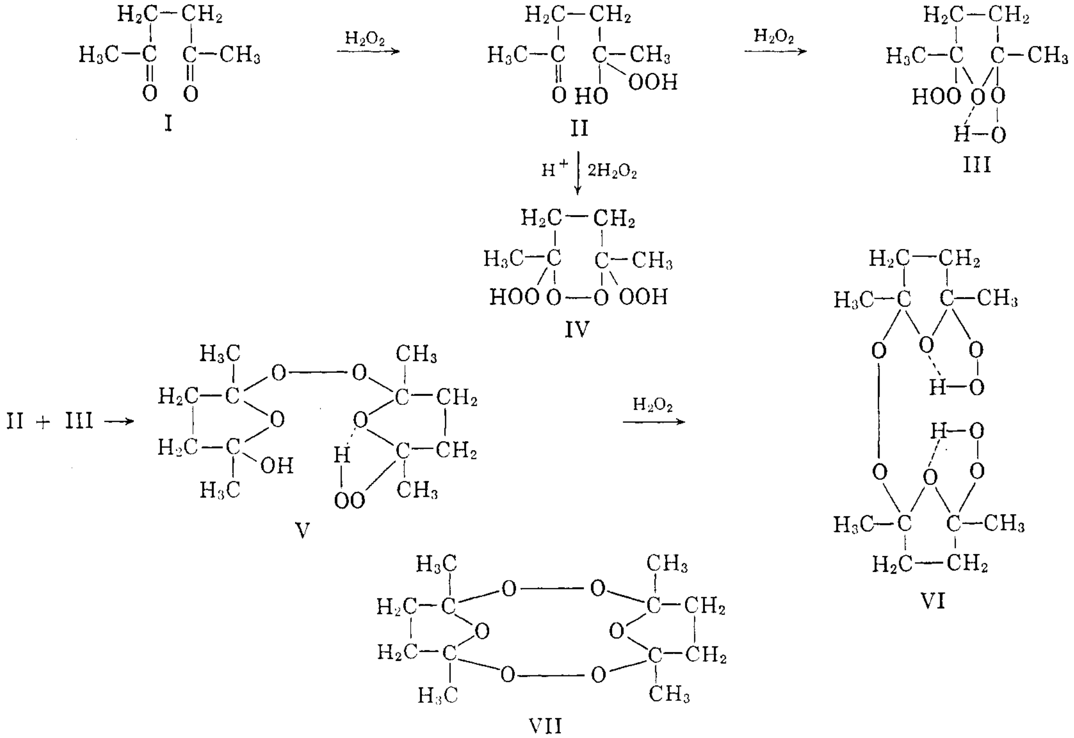

Fig. 2.—Tentative structural assignments of peroxides derived from 2,5-hexanedione and hydrogen peroxide in the presence or absence of mineral acids.

gen of 19.5% and an infrared spectrum which showed strong hydrogen bonding. All attempts to crystallize it from organic solvents were unsuccessful. However, in an attempt to crystallize it from water, it underwent a quantitative conversion to peroxide VI. Moreover, when it was subjected to a prolonged high vacuum (0.1 mm.) pumping at 50°, it again was converted to peroxide VI. Furthermore, when it was dissolved in anhydrous ether and the solution treated at low temperatures with phosphorus pentoxide, peroxides VI and VII were formed in yields of 10 and 70%, respectively. Although the active oxygen of peroxide R_f 0.00 is in close. agreement with that calculated for peroxide III,

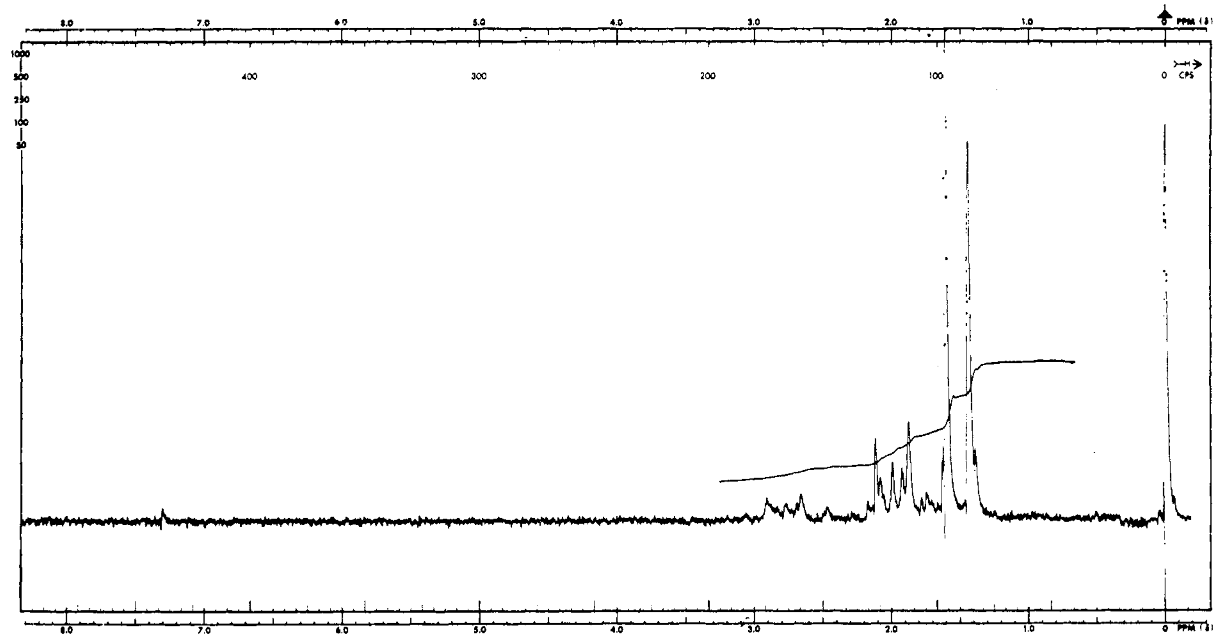

Fig. 3a.—N.m.r. spectrum of the bicyclic peroxide VII 13.5% in deuteriochloroform taken at 60 Mc./sec. Only chemical shifts attributed to CH_3 and CH_2 groups are visible.

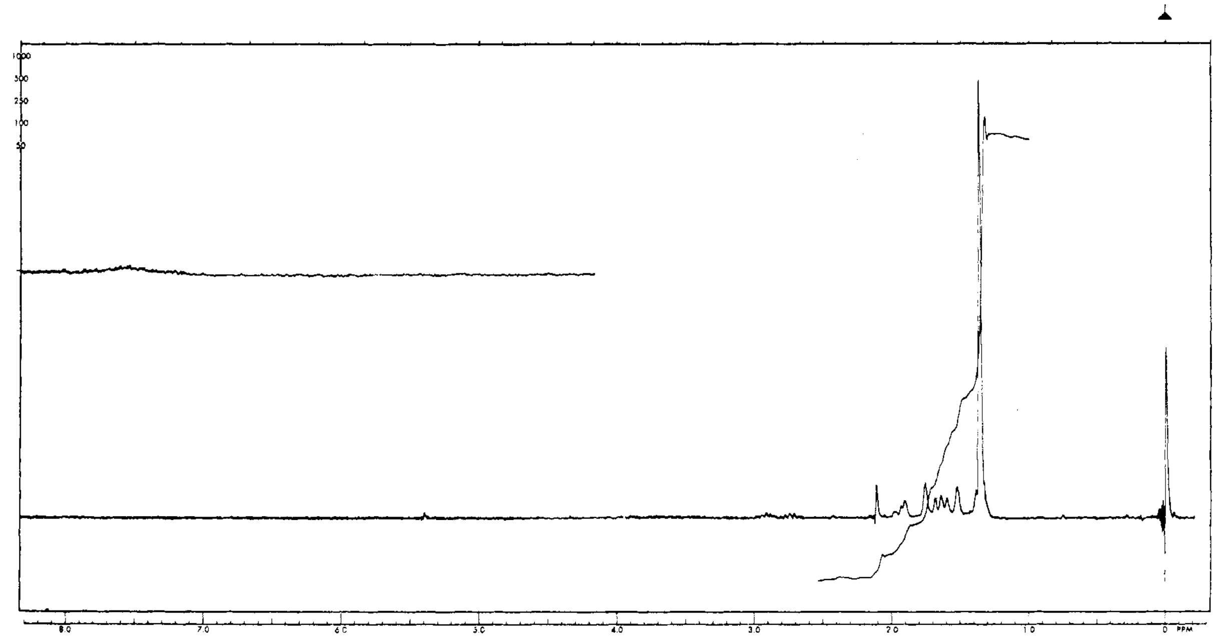

Fig. 3b.—N.m.r. spectrum of the dihydroperoxy peroxide IV 23.5% in $DCON(CD_3)_2$ taken at 60 Mc./sec. Chemical shifts at 10.75–10.91 p.p.m. are due to weak hydrogen bonding of the hydroperoxy groups while the band at 2.1 p.p.m. may be due to the protons of hydroperoxy groups. The other chemical shifts are due to CH_3 and CH_2 groups, respectively.

its conversion to peroxides VI and VII indicates that it must be a mixture of the unidentified peroxide V and hydrogen peroxide which could not be removed with ammonium sulfate.

When the reaction of 2,5-hexanedione and hydrogen peroxide was carried out at 0° in the presence of 1% sulfuric acid, the course of the reaction was different and a six-membered ring dihydroperoxy peroxide (IV) was the only peroxide isolated (Fig. 2). Analytical data, molecular weight, and infrared spectra seem to favor structure IV. Additional support for this structure was supplied by the preparation of its bis-*p*-nitrobenzoate, which gave the correct analysis and molecular weight. An infrared spectrum of a mull in Nujol of this derivative showed a strong perester band at 1765–1760 cm.$^{-1}$ and no bands in the hydroperoxy region. The n.m.r. spectrum of this peroxide in $DCON(CD_3)_2$ (Fig. 3b) shows the absence of vinylic hydrogen, but it is somewhat difficult to make definite assignments for all the signals except those due to —CH_2— and —CH_3 groups.

Experimental

All n.m.r. spectra were run on a Varian A-60 high resolution n.m.r. spectrometer at a frequency of 60 Mc./sec. The samples were run in deuteriochloroform and $DCON(CD_3)_2$ solutions, the concentrations of which are recorded with the spectra in Fig. 1 and 3.

Reaction of 2,5-Hexanedione (Acetonylacetone) with Hydrogen Peroxide.—To 40.8 g. of 50% hydrogen peroxide maintained at 0° was added dropwise with rapid stirring in the course of 1 hr., 34.4 g. of acid-free freshly distilled 2,5-hexanedione. The reaction mixture was allowed to warm to room temperature and kept under these conditions for 4 days. A chromatogram taken of the crude mixture, using hydrogen iodide–glacial acetic acid as the detecting agent, showed the presence of five different peroxides. The percentage of each peroxide was estimated from the intensity of its R_f to be approximately R_f: 0.00, 85%; 0.09, traces; 0.220, 9%; 0.350, traces; 0.665, 6%.

The reaction mixture was transferred to a separatory funnel and extracted with pentane (200 ml.). A paper chromatogram of the pentane solution showed the presence of all the spots of the original mixture except the one with R_f 0.00. The pentane solution then was washed successively with a saturated solution of ammonium sulfate and water, dried, and filtered. When the filtrate was cooled to −70°, colorless crystals separated which were recrystallized several times from pentane. A paper chromatogram taken of the crystals (m.p. 132°) showed a very strong spot with R_f, 0.220 and minute trace spots with R_f 0.09 and 0.350. A chromatogram of the mother liquors likewise showed a very strong spot with R_f 0.665 and small trace spots with R_f 0.09 and 0.350.

Both the crystals and the mother liquor therefore were subjected to cellulose powder chromatography using the same technique previously published from this laboratory.[5] From these crystals was obtained peroxide VI which gave a single strong spot on a paper chromatogram with an R_f 0.220; m.p. 135°.

Anal. Calcd. for $C_{12}H_{22}O_8$ (VI): C, 48,98; H, 7.53; O, 16.31; mol. wt., 294.3. Found: C, 49.20; H, 7.56; O, 16.28 (KI + CH_3COOH method); mol. wt., 292 (cryoscopic in dioxane).

The infrared spectrum 10% in chloroform showed the following principal bands in cm.$^{-1}$: 3400(8); 2998(5); 2980(3.5); 1455(6.5); 1440(6.5); 1410(6); 1378(9.3); 1330(4.5); 1308(4.4); 1280(6); 1205–1234(8.5); 1110-(9); 1100(9.5); 1085(8.5); 1058(8.2); 985(7.3); 915(7); 900(6.5); 870(8.9); 850(8.9). The n.m.r. spectrum measured in deuteriochloroform is recorded in Fig. 1.

Using the Brewster–Cotte procedure,[6] the bis-*p*-nitrobenzoate was prepared from peroxide VI in 30% yield; m.p. 105° (explosive) from methyl alcohol.

Anal. Calcd. for $C_{26}H_{28}N_2O_{14}$: C, 52.70; H, 4.76; N, 4.73; mol. wt., 592.5. Found: C, 52.74; H, 4.95; N, 4.79; mol. wt., 586 (cryoscopic in dioxane).

The infrared spectrum of a mull in Nujol of this derivative showed a strong band at 1766–1760 cm.$^{-1}$ due to the perester groups, two bands at 850 and 870 cm.$^{-1}$, respectively due to the —O—O— groups, and no bands in the hydroperoxy region.

When the mother liquor mentioned above was subjected to cellulose powder chromatography, peroxide VII was obtained free from traces of other peroxides. It showed a single strong spot on a paper chromatogram, using hydrogen iodide and glacial acetic acid as the detecting agent, with an R_f 0.665; m.p. 105° dec.

Anal. Calcd. for $C_{12}H_{20}O_6$ (VII): C, 55.38; H, 7.74; O, 12.30; mol. wt., 260.3. Found: C, 55.47; H, 7.72; O, 12.80; mol. wt., 260 (in exaltone).

The infrared spectrum 10% in chloroform showed the following principal bands in cm.$^{-1}$: 2998(8); 2980(6); 2850(3); 1455(7); 1445(7); 1378(9.3); 1330(4.5); 1315-(8.3); 12756(6); 1240(7.8); 1210–1230(7); 1190(9.2); 1130(9.8); 1110(9.8); 1082(4); 1050(9); 995(9.2); 925(8); 885(9); 970(9). The n.m.r. spectrum of this peroxide in deuteriochloroform is recored in the upper part of Fig. 3a.

Peroxide VII reacts very slowly with potassium iodide in glacial acetic acid, and since its infrared spectrum shows no hydroxyl groups, the conclusion may be drawn that it may have a cyclic structure best represented by formula VII.

Purification of Peroxide with R_f, 0.0.—The aqueous layer from the original mixture, after the pentane extraction, contained all of the peroxide (*ca.* 85%) with R_f 0.00. It was extracted with two 100-ml. portions of ethyl ether and the ether extracts washed with two 50-cc. portions of saturated ammonium sulfate, then once with water, dried, and the ether removed *in vacuo* (50 mm.), leaving a colorless viscous oil. This oil had an active oxygen of 19.5%. Attempts to crystallize the oil from ether, dichloromethane, and other solvents were not successful. A paper chromatogram gave a single strong spot which failed to move from the origin, with traces of peroxides with R_f: 0.09, 0.220, and 0.665. An attempt was made to dissolve this peroxide in water when all of it precipitated as a white solid; m.p. 110° (after drying *in vacuo*). When this was subjected to cellulose column chromatography, more than 85% was obtained having an R_f 0.220 (peroxide VI) and m.p. 135°.

Moreover, when the oily peroxide with R_f, 0.00 was subjected to prolonged high vacuum (0.1 mm.) at 50°, it was converted completely to peroxide VI which could be obtained pure by a single crystallization from ether without the use of cellulose column chromatography. Furthermore, since the peroxide with R_f, 0.00 in the original mixture was the only peroxide detected when the ratio of acetonylactone to hydrogen peroxide used was 1 to 4, it was possible to obtain peroxide VI by the above conversion in nearly quantitative yields.

Reaction of Peroxide, R_f, 0.00 with Phosphorus Pentoxide.—A solution of 100 mg. of peroxide, R_f 0.00 in 100 ml. of anhydrous ether, was cooled to 0° and to it was added with frequent shaking in the course of 8 hr., 2 g. of phosphorus pentoxide in eight equal portions. The final mixture was filtered into a separatory funnel and washed with 50 ml. of saturated sodium bicarbonate, dried, and concentrated to about one quarter its volume. Using a paper chromatogram, the following peroxides were estimated from the intensity of their spots to be present in the solution: peroxide VII, R_f 0.665, 70%; peroxide VI, R_f 0.220, 10%; and unreacted peroxide, R_f 0.00, 20%.

Reaction of 2,5-Hexanedione with Hydrogen Peroxide in the Presence of 1% Sulfuric Acid.—To 27.2 g. (0.4 mole) of 50% hydrogen peroxide containing 1% sulfuric acid and cooled to 0° was added in the course of 0.5 hr. with rapid stirring 11.4 g. (0.1 mole) of freshly distilled 2,5-hexanedione. The mixture was allowed to stand at 0° for 3 hr., then at room temperature for 4 days whereby white crystals separated and removed by filtration; yield, 31.7%. This was recrystallized from dichloromethane into long needles, m.p. 131°. This peroxide is very sensitive to shock and explodes with considerable brisance.

Anal. Calcd. for $C_6H_{12}O_6$ (IV): C, 40.01; H, 6.71; O, 26.64; mol. wt., 180.2. Found: C, 40.16; H, 6.65; O, 26.50 (KI + CH_3COOH method); mol. wt., 181.4 (cryoscopic in dioxane).

The infrared spectrum of a mull in Nujol showed the following bands in cm.$^{-1}$: 3300(8.5); 2885–2995(9.8); 1445-(9.3); 1370(9.2); 1340(6.5); 1270(7.2); 1245(5.3); 1155-(7.8); 1110–1120(8.2); 1060(7.5); 1020(4.5); 960(5); 935-(4); 920(5.5); 890(4.5); 865(8). The n.m.r. spectrum of this peroxide in $DCON(CD_3)_2$ is recorded in Fig. 3b.

The bis-*p*-nitrobenzoate ester of the above dihydroperoxy peroxide was prepared according to Brewster and Cotte[6]; yield, 78.7%; m.p. 165° dec. from absolute ethyl alcohol.

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(6) J. H. Brewster and C. J. Cotte, Jr., *J. Am. Chem. Soc.*, **77**, 6214 (1955).

Anal. Calcd. for $C_{20}H_{18}N_2O_{12}$: N, 5.86; O, 10.03. mol. wt., 478.4. Found: N, 5.96; O, 10.42; mol. wt., 480 (cryoscopic in dioxane).

This derivative was too explosive for carbon and hydrogen analyses. An infrared spectrum of a mull in Nujol showed a strong band at 1765–1760 cm.$^{-1}$ due to the perester groups, and two bands at 850 and 870 cm.$^{-1}$, due to the —O—O— groups, and no bands in the hydroperoxy region.

Acknowledgment.—The authors wish to thank Dr. S. M. Nagy for all the combustion analyses, Dr. P. H. Niklaus for the n.m.r. spectra, Miss Jessie C. J. Ho for technical assistance, and the Lucidol Division of Wallace and Tiernan, Inc., and Research Corporation for financial support of this investigation.

Selective Semihydrogenation of Tertiary Ethynylcarbinols in the Presence of Base

ROBERT J. TEDESCHI AND GEORGE CLARK, JR.

Research Laboratories, The Air Reduction Chemical Company, Murray Hill, New Jersey

Received June 21, 1962

An improved method for the semihydrogenation of tertiary ethynylcarbinols has been developed. Low pressure hydrogenations in the presence of bases such as potassium hydroxide, sodium hydroxide, sodium methoxide, and alkali metals using palladium, platinum, or rhodium catalysts on carriers such as charcoal, barium carbonate, calcium carbonate, or barium sulfate yield vinylcarbinols in good yield (77–92%) and purity (95–97%). A catalyst to base weight ratio of 1:1 to 1:2 is employed. In the absence of base, vinylcarbinols of lower purity (82–88%), contaminated with the corresponding ethynyl and saturated carbinols are obtained. Unprotected hydrogenations also show no tendency to halt selectively. The catalyst system of palladium on barium carbonate in the presence of powdered potassium hydroxide was found to be the most useful studied.

The partial hydrogenation of tertiary ethynylcarbinols has been discussed by Johnson[1] and K. N. Campbell.[2] Palladium[3] and Raney nickel catalysts[4,5] have been used frequently in this operation and were claimed to be selective for the semihydrogenation of the triple bond. This selective action involves not only the specific hydrogenation of the acetylenic to vinylcarbinol but also the halting of further hydrogenation after all the acetylenic has been converted to ethylenic derivative. The unsaturated carbinol should be absent or present in a very small amount. Raphael[6] has pointed out that in recent years palladium has come to be regarded as the most useful catalyst for semihydrogenation. However, the development of the Lindlar catalyst[7] (palladium on calcium carbonate inactivated with lead acetate and quinoline) demonstrated that palladium without a suitable inhibitor does not always show selective action. Recently Hennion and co-workers[8] claimed a selective technique for the semihydrogenation of tertiary ethynyl carbinols using very small amounts of palladium on barium carbonate catalyst.

Attempts in this laboratory to prepare tertiary vinylcarbinols in 95% or better purity by the Lindlar or the Hennion method were unsuccessful. The resulting product was always contaminated with varying amounts of unreduced acetylenic and an equal amount of saturated carbinol. The longer the chain length of the starting material the less selective the hydrogenation became showing also no tendency to stop selectively at the end of the first stage ($-\mathrm{C{\equiv}C}= \rightarrow -\mathrm{CH{=}CH}-$) of hydrogenation.

While investigating[9] the hydrogenation and hydrogenolysis of tertiary 1,4-acetylenic glycols, it was observed that small amounts of alkali metal base eliminated hydrogenolysis, and also inhibited the more rapid rate of hydrogenation of the first stage, although complete cessation of hydrogenation was not observed. While hydrogenolysis was found to be an insignificant side reaction for the tertiary ethynyl and vinyl carbinols, the above results indicated that increased amounts of base might also function as an inhibitor for the more rapid first stage of carbinol hydrogenation, and show selectivity for producing pure tertiary vinylcarbinols. Also, the known instability of the tertiary ethynylcarbinols to base at higher temperatures might be useful in the preparation of pure vinylcarbinols by cleaving unchanged ethynylcarbinols into acetylene and lower boiling ketone.

The systematic use of potassium hydroxide or sodium hydroxide with a variety of tertiary acetylenic carbinols was found to give distilled vinylcarbinols of 95–97% minimum purity in good yield (77–92%). Hydrogenation under the same

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(1) A. W. Johnson, "Acetylenic Compounds," Vol. I, "The Acetylenic Alcohols," Edw. Arnold Co., London, 1946, pp. 90–91, 131, 207.

(2) K. N. Campbell and B. K. Campbell, *Chem. Rev.*, **31**, 77 (1942).

(3) M. Bourgel, *Bull. Soc. Chim.* (4) **41**, 1443, 1475 (1927); **45**, 1667 (1929); **51**, 253 (1932); M. Bourgel and V. Gredy, *Compt. rend.*, **189**, 757 (1929); V. Gredy, *Bull. Soc. Chim.*, (5) **2**, 1029 (1935).

(4) G. DuPont, *ibid.*, (5) **3**, 1030 (1936).

(5) K. N. Campbell and M. J. O'Conner, *J. Am. Chem. Soc.*, **61**, 2897 (1939).

(6) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press, Inc., New York, N. Y., 1955, pp. 23, 200.

(7) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952); U.S. Patent 2,681,938 (June 22, 1954).

(8) G. F. Hennion, *et al.*, *J. Org. Chem.*, **21**, 1142 (1956).

(9) R. J. Tedeschi, *ibid.*, **27**, 2398 (1962); U.S. Patent 2,992,278 (July 11, 1961).