

**2-Carboethoxycycloheptanone.**—In a similar manner, 33.5 g. (0.18 mole) of the morpholine enamine of cycloheptanone and 11.0 g. (0.102 mole) of ethyl chloroformate in 150 ml. of dry benzene gave 7.35 g. (46%) of  $\beta$ -keto ester, b.p. 110–125° (10 mm.), reported<sup>91</sup> b.p. 125–126° (12 mm.); phenylpyrazolone, m.p. 210–214° (reported<sup>92</sup> m.p. 210°).

**2-Carboethoxypentanone-3.**—In a similar manner, 25.0 g. (0.16 mole) of the morpholine enamine of diethyl ketone and 9.0 g. (0.083 mole) of ethyl chloroformate in 150 ml. of dry benzene gave 4.6 g. (37%) of  $\beta$ -keto ester, b.p. 87–97° (12 mm.). The phenylpyrazolone was prepared from the carboethoxy ketone by reaction with phenylhydrazine; m.p. 109–110.5° (reported<sup>93</sup> 112.5°).

**3-Carboethoxyheptanone-4 (LXVIII).**—In a similar manner, 25.0 g. (0.136 mole) of the morpholine enamine of dipropyl ketone and 9.0 g. (0.083 mole) of ethyl chloroformate in 150 ml. of dry benzene gave 6.7 g. (53.3%) of  $\beta$ -keto ester, b.p. 105–106° (15 mm.) (reported<sup>94</sup> b.p. 88–90° (12 mm.)).

(91) V. Prelog and W. Hinden, *Helv. Chim. Acta*, **27**, 1854 (1944).

(92) W. Dieckmann, *Ber.*, **55**, 2470 (1922).

(93) O. Emmerling and L. Kristeller, *ibid.*, **39**, 2452 (1906).

(94) J. C. Shivers, M. L. Dillon and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 119 (1947).

**2-Carboethoxycyclohexanone by Reaction in the Presence of Diethylaniline.**—The morpholine enamine of cyclohexanone (16.7 g., 0.10 mole) and diethylaniline (16.4 g., 0.11 mole) were dissolved in 100 ml. of chloroform and, while the system was kept under a nitrogen atmosphere, ethyl chloroformate (12.0 g., 0.11 mole) was added and the mixture was refluxed for 7 hours. The solution was then transferred to a separatory funnel and 3 ml. of concentrated hydrochloric acid in 35 ml. of water was added. The mixture was shaken at intervals over a period of 15–30 minutes. The layers were then separated, and the chloroform solution was washed successively with two 25-ml. portions of 10% hydrochloric acid and four 25-ml. portions of water. These wash solutions and the original hydrochloric acid solution were combined and extracted with three 50-ml. volumes of benzene. The benzene extracts and chloroform solution were combined and dried over anhydrous sodium carbonate. After filtration from drying agent (which was washed with dry benzene) solvent was removed from the filtrate by atmospheric pressure distillation. Fractionation of the residue through a short-path column gave 9.47 g. (56%) of product, b.p. 100–110° (10 mm.). The infrared spectrum of this compound was identical with that of authentic 2-carboethoxycyclohexanone.

Under the same conditions but with one equivalent of triethylamine instead of diethylaniline no  $\beta$ -keto ester could be obtained.

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## Studies in Organic Peroxides. XXIX. The Structure of Peroxides Derived from 2,4-Pentanedione and Hydrogen Peroxide<sup>1</sup>

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2,4-Pentanedione (II) reacts at 0° with one mole of hydrogen peroxide to form 3,5-dimethyl-3,5-dihydroxy-1,2-peroxycyclopentane (IV) or 3,5-dimethyl-3,5-dihydroxy-1,2-dioxolane. When the same reaction is carried out with two moles of hydrogen peroxide, 3,5-dimethyl-3-hydroxy-5-hydroperoxy-1,2-peroxycyclopentane (V) is formed. With three moles of hydrogen peroxide in dilute acid solutions, II yields 3,5-dimethyl-3,5-dihydroperoxy-1,2-peroxycyclopentane (VI). Peroxide V can be converted either in dilute aqueous acid solution or in anhydrous ether with phosphorus pentoxide to the bicyclic peroxide VII. Peroxide VI forms readily a crystalline bis-*p*-nitrobenzoate. The infrared spectra of all peroxides in this group have been measured by the mull method and in dimethoxyethane. The ultraviolet spectra of peroxides IV and V in dilute solution show considerable dissociation to their original components. The dissociation of peroxide IV in dilute ether and chloroform solutions is a monomolecular reaction. The n.m.r. spectra of all peroxides in this group were measured in CDCl<sub>3</sub>, CD<sub>3</sub>OD and D<sub>2</sub>O solutions. It has been found that the undissociated peroxide IV exists in solution as a 2:3 mixture of *cis* and *trans* isomers, although in the solid state it may exist as a single isomer which is equilibrated in solution to the 2:3 mixture. Peroxides V and VI exist only as the *trans* isomers while by reason of its symmetry the bicyclic peroxide VII exists only in the *cis* configuration.

In previous publications<sup>5a,b,c</sup> we have described several organic peroxides derived from the reaction of simple aliphatic monoketones and hydrogen peroxide. The present communication deals with the preparation and structure of peroxides derived from the reaction of hydrogen peroxide and 2,4-pentanedione. When diketone II was allowed to react at 0° with one mole of 50% hydrogen peroxide, a crystalline peroxide was formed in the course of 4 hr.  $\pm$  5 min. in yields of 90–92%. The analytical data for this peroxide support either structure III or IV. However, infrared spectra taken by the mull method<sup>6</sup> in Nujol or 10% in dimethoxyethane<sup>7</sup> failed to show a carbonyl band; we are therefore in favor of structure IV. Moreover, the n.m.r. spectra show also no evidence for the presence of peroxide III. The strong infrared bands near 1080 and 1160 cm.<sup>-1</sup>, respectively, may be attributed to 1,3-diols,<sup>8</sup> while the region 1150–1080 cm.<sup>-1</sup> has also

been attributed to ketals<sup>9</sup> in which two oxygen atoms are attached to the same carbon atom, as in the case of the peroxides described in this paper.

In spite of its stability at room temperature, when peroxide IV was heated in a long tube at the b.p. of acetone and at a pressure of about 2 mm., it appeared to dissociate to its original components which recombined in the cold part of the tube to form a crystalline peroxide of much less purity, and a liquid which was collected in a trap immersed in Dry Ice–acetone mixture. The liquid showed the presence of both free hydrogen peroxide (silver foil test) and 2,4-pentanedione.

The hydroxyhydroperoxyperoxide V was obtained either by adding one mole of hydrogen peroxide to the dihydroxyperoxide IV or by adding directly two moles of hydrogen peroxide to 2,4-pentanedione. This peroxide had essentially the same infrared spectrum as peroxide IV except in the hydroxyl region, 3230–3430 cm.<sup>-1</sup>, where it showed a doublet due perhaps to the difference in the structure of the two groups attached to carbon atoms 3 and 5. Similarly, the dihydroperoxyperoxide VI was obtained either by adding one mole

(1) Since our original manuscript was submitted Jan. 19, 1961, a paper appeared on the same subject by A. Rieche and C. Bischoff, *Chem. Ber.*, **95**, 77 (1962).

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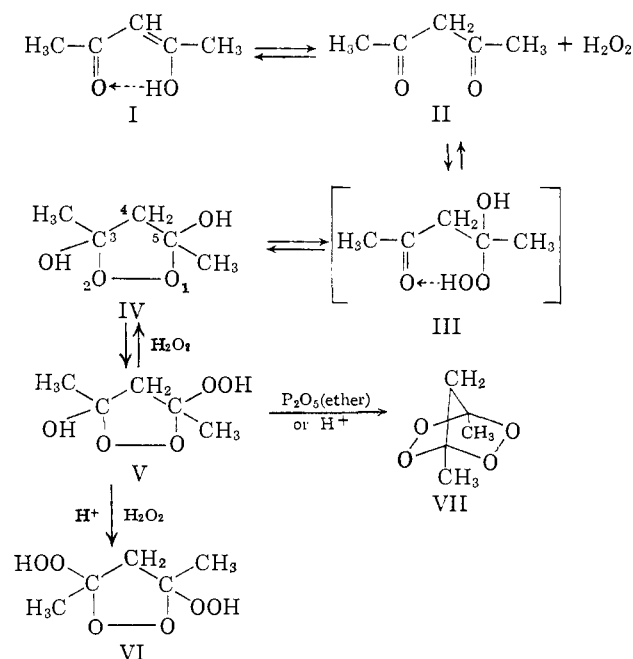
(5) N. A. Milas and A. Golubović, *J. Am. Chem. Soc.*, **81**, (a) 3361; (b) 5824; (c) 6461 (1959).

(6) J. P. Wibaut and Th. J. De Boer, *Rec. trav. chim.*, **78**, 183 (1959).

(7) Dimethoxyethane was the only suitable solvent for infrared measurement of this peroxide in the hydroxyl and carbonyl regions.

(8) E. Nagai, S. Kuribayashi, M. Shiraki and M. Ukita, *J. Polymer. Sci.*, **35**, 295 (1959).

(9) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 116.



of hydrogen peroxide to peroxide V, two to peroxide IV or three to 2,4-pentanedione, all in the presence of small amounts of sulfuric acid. Moreover, small amounts of peroxide VII were also separated from the reaction products.

Peroxide VII was prepared in higher yields by the direct dehydration of peroxide V with phosphorus pentoxide in ether.

**Ultraviolet Absorption Measurements.**—A study of the ultraviolet spectra of this group of peroxides in solution showed that peroxides IV and V dissociate into their original components. The rate of dissociation of these peroxides as well as the rate of their formation in dilute solutions in ether and water was studied spectroscopically and the results are recorded in Tables I, III and IV. The rate of dissociation of peroxide IV in ether and chloroform solutions at room temperature is a first-order reaction (Tables I and II). However, peroxide V shows no ultraviolet absorption in ether and even in dilute aqueous solutions the dissociation is very low. Since peroxides VI and VII showed no absorption in the ultraviolet, we have made the assumption in our calculations that the only component that absorbs in this region is the enol or chelated form (I) of 2,4-pentanedione. Conant and Thompson,<sup>10</sup> reported that at 25° 2,4-pentanedione in a 0.1 M solution in hexane is 91.4–92% or 91.7% in the enol or chelated form. More recently, Eistert and Reiss<sup>11</sup> have measured the ultraviolet absorption of this diketone in heptane and reported an  $\epsilon$ -value at 270 m $\mu$  of 11,000. Using the values of Conant and Thompson and Eistert and Reiss we have found that a water solution at 25° containing  $3 \times 10^{-4}$  mole per liter of 2,4-pentanedione has an  $\epsilon$ -value at 275 m $\mu$  of 1930 or 16.1% as the chelated form, a value which is in close agreement with the value of 15.5% reported at 20° by Schwarzenbach and Felder.<sup>12</sup>

From the results of Tables I and III one can easily draw the conclusion that in dilute ether solutions peroxide IV is nearly completely dissociated to its original components after about five hours, and hydrogen peroxide in the same solvent does not react with the chelated ketone, as judged by the constant  $K_2$ , the ratio of the chelated ketone, as determined spectroscopically, to

(10) J. B. Conant and A. F. Thompson, Jr., *J. Am. Chem. Soc.*, **54**, 4039 (1932).

(11) B. Eistert and W. Reiss, *Chem. Ber.*, **87**, 108 (1954).

(12) G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

TABLE I  
DISSOCIATION OF 3,5-DIMETHYL-3,5-DIHYDROXY-1,2-PEROXYCYCLOPENTANE (IV) IN ETHYL ETHER AT 25 ± 1°

Time, min.	$\epsilon$ (λ, 270–272 m $\mu$ )	Chelate, %	$C_0$ , moles/l. $\times 10^{-4}$	$x$ , moles/l. $\times 10^{-4}$	$C_0 - x$ , moles/l. $\times 10^{-4}$	$K_1 \times 10^{-4}$
10	927	7.73	34.63	2.68	31.95	8.1
25	2606	21.73	34.63	7.52	27.11	9.8
35	3520	29.35	34.63	1.016	2.447	9.9
70	5975	49.81	34.63	1.725	1.738	9.8
100	6700	55.85	34.63	1.934	1.529	8.1
150	8404	70.06	34.63	2.426	1.037	8.0
180	8870	73.95	34.63	2.561	0.902	7.5
300	9906	82.58	34.63	2.86	0.603	5.9
					Mean	8.2

TABLE II  
DISSOCIATION OF 3,5-DIMETHYL-3,5-DIHYDROXY-1,2-PEROXYCYCLOPENTANE (IV) IN CHLOROFORM AT 25 ± 1°

Time, min.	$\epsilon$ (λ, 274 m $\mu$ )	Chelate, %	$C_0$ , moles/l. $\times 10^{-4}$	$x$ , moles/l. $\times 10^{-4}$	$C_0 - x$ , moles/l. $\times 10^{-4}$	$K_1 \times 10^{-4}$
45	319	2.69	15.23	0.410	14.82	5.5
60	438	3.66	3.81	.139	3.671	6.2
135	694	5.79	3.81	.221	3.589	4.4
240	982.5	8.20	3.81	.312	3.498	3.6
330	1232	10.30	3.81	.392	3.418	3.3
450	1480	12.32	3.81	.470	3.340	3.0
570	1702	14.20	3.81	.555	3.255	2.9
720	1943	16.20	3.81	.62	3.19	2.5
					Mean	4.0

TABLE III  
ULTRAVIOLET SPECTROSCOPIC MEASUREMENTS IN ETHYL ETHER OF 2,4-PENTANEDIONE AND OF MIXTURES OF THIS KETONE AND HYDROGEN PEROXIDE AT 25 ± 1°

Time, min.	$\epsilon$ (270–272 m $\mu$ )	Chelated ketone, %	$C_0$ , concn. of ketone, moles/l. $\times 10^{-4}$	$x$ , concn. of di-chelated ketone, moles/l. $\times 10^{-4}$	$C_0 - x$ , concn. of un-chelated ketone, moles/l. $\times 10^{-4}$	$K_2 = \frac{x}{C_0 - x}$	Average
30	9915	82.66	42.7	35.30	7.40	4.70	5.06
1440	9975	83.16	42.7	36.05	6.65	5.42	
2,4-Pentanedione H <sub>2</sub> O <sub>2</sub> (mole:mole) in ethyl ether							
30	9965	83.07	57.26	47.57	9.69	4.91	4.82
1440	9903	82.56	57.26	47.27	9.99	4.73	
2,4-Pentanedione:H <sub>2</sub> O <sub>2</sub> (mole:2 moles) in ethyl ether							
30	9990	83.28	57.35	47.76	9.59	4.98	4.84
1440	9893	82.47	57.35	47.30	10.05	4.71	
2,4-Pentanedione:H <sub>2</sub> O <sub>2</sub> (mole:3 moles) in ethyl ether							
30	10030	83.61	57.35	47.95	9.40	5.10	4.86
1440	9858	82.18	57.35	47.13	10.22	4.61	
From Table I, peroxide IV in ethyl ether							
300	9906	82.58	34.63	28.60	6.03	4.74	4.74

the unchelated diketone which may exist either as the free diketone or as peroxides III or IV. Furthermore, these results as well as those of Table II seem to indicate that infrared spectra of hemiperketals or  $\alpha$ -hydroxyhydroperoxides are not reliable when measured in solution due to their slow dissociation. This fact has been known for some time<sup>13</sup> and for this reason the null method has been recommended.<sup>6</sup>

The behavior of peroxides IV and V in dilute water solutions as well as that of mixtures of hydrogen peroxide and 2,4-pentanedione is somewhat different

(13) E. G. E. Hawkins, "Organic Peroxides," E. and F. F. Spon Ltd., London, 1961, Chapter V, p. 137.

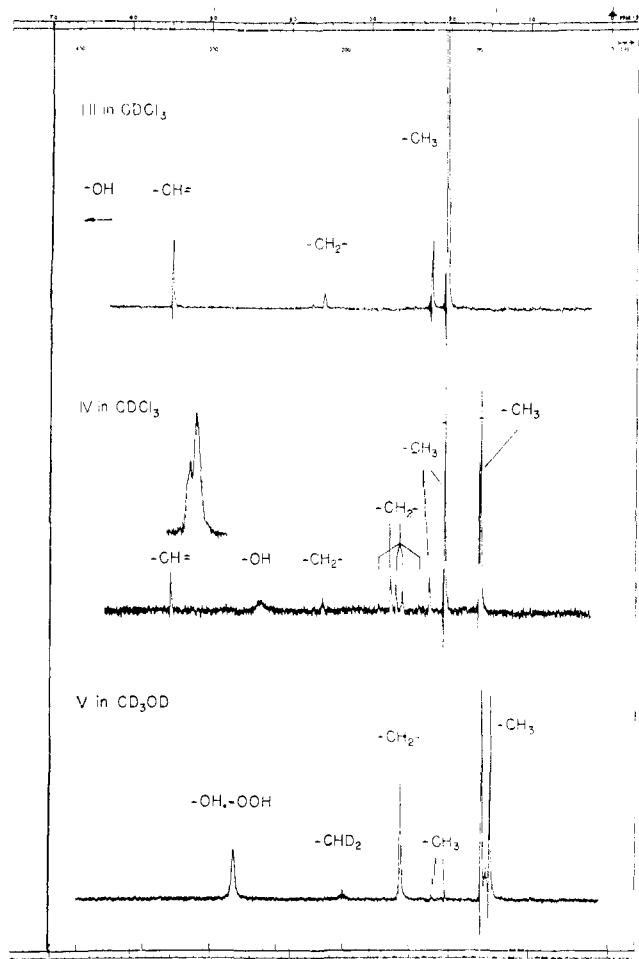


Fig. 1.—N.m.r. spectra of acetylacetone and peroxides IV and V. The presence of acetylacetone in solutions of peroxides IV and V is clearly visible.

(Table IV). Even the pure 2,4-pentanedione, alone in water, exists mainly as the diketone, and since peroxide IV, the precursor of all other peroxides isolated, is formed in high yields in water, then hydrogen peroxide must react with the diketone or its monohydrated form rather than with the chelated form of this ketone.

**Nuclear Magnetic Resonance Spectra.**<sup>14</sup>—Ultra-violet and infrared spectroscopic measurements of peroxide IV at room temperature in different solvents have already shown that it dissociates into its original components. Although peroxide V undergoes slow dissociation in aqueous solutions, it is stable for long periods of time in ether. Peroxides VI and VII, on the other hand, are stable in all of the solvents investigated. Confirmation of these findings and additional information regarding the stereochemistry of these peroxides were sought in a study of their n.m.r. spectra. Some of the spectra which were run in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$  and  $\text{D}_2\text{O}$  solutions are recorded in Fig. 1. In the case of peroxides IV and V the interpretation of the results is somewhat involved due to their dissociation in solution and partial and incomplete deuteration by exchange reactions. Methyl resonances have been found to occur at 1.5–1.7 p.p.m.<sup>15</sup> if attached to the peroxide ring and at 2.0–2.3 p.p.m. if attached to acetylacetone. Similarly, the methylene resonance is

(14) All spectra were run on a Varian A-60 high resolution NMR spectrometer at a frequency of 60 Mc./s. The samples were run 10% in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$  and  $\text{D}_2\text{O}$  except peroxide IV which was run 2–3% in  $\text{CDCl}_3$ . Tetramethylsilane was used as internal standard in  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  solution.

(15) Line positions are given in parts per million (p.p.m.) downfield from the absorption of tetramethylsilane.

TABLE IV

ULTRAVIOLET SPECTROSCOPIC MEASUREMENTS IN WATER OF PEROXIDE IV AND V AND OF MIXTURES OF 2,4-PENTANEDIONE AND HYDROGEN PEROXIDE AT  $25 \pm 1^\circ$

Time, min.	$\epsilon$ (275 m $\mu$ )	Chelated ketone, %	$C_0$ , moles/l. $\times 10^{-3}$	$x$ , moles/l. $\times 10^{-3}$	$C_0 - x$ , moles/l. $\times 10^{-3}$	$K_2 = \frac{x}{C_0 - x} \times 10^{-3}$
Peroxide IV in Water						
30	1750	14.59	18.96	2.77	16.19	17.11
1440	868.3	7.24	18.96	1.37	17.59	7.80
Peroxide V in water						
30	135	1.13	105.3	1.20	104.10	1.15
1440	148	1.23	105.3	1.30	104.00	1.25
2,4-Pentanedione:H <sub>2</sub> O <sub>2</sub> (mole:mole) in water						
30	1093	9.11	22.7	2.10	20.60	10.20
1440	766	6.39	22.7	1.45	21.20	6.84
2,4-Pentanedione:H <sub>2</sub> O <sub>2</sub> (mole: 2 moles) in water						
30	782	6.52	25.27	1.65	23.62	7.00
1440	131	1.10	25.27	0.28	24.99	1.10
30	792	6.60	29.40	1.94	27.46	7.10
1440	190	1.58	29.40	0.46	28.94	1.59
2,4-Pentanedione:H <sub>2</sub> O <sub>2</sub> (mole:3 moles) in water						
30	597	4.98	48.96	2.44	46.52	5.30
1440	141	1.18	48.96	0.58	48.38	1.20
30	593	4.94	36.32	1.79	34.53	5.20
1440	144	1.20	36.32	0.43	35.89	1.20
2,4-Pentanedione:H <sub>2</sub> O <sub>2</sub> (mole:4 moles) in water						
30	498	4.15	47.60	1.97	45.63	4.30
1440	95.5	0.80	47.60	0.38	47.22	0.80

at 2.6–2.8 p.p.m. for the peroxide ring and at 3.5–3.7 for acetylacetone.

Spectra of acetylacetone have been recorded and interpreted elsewhere.<sup>16</sup> It may be mentioned here, however, that for the  $\text{D}_2\text{O}$  spectrum of this compound no vinylic proton resonance could be observed, an indication of complete deuteration in that position. The  $\text{CDCl}_3$  spectrum of peroxide IV shows clearly the presence of chelated and unchelated 2,4-pentanedione (lines of vinylic, methylene and methyl protons). The methyl resonance of this peroxide shows two very close lines and the methylene resonance consists of a single line and an AB-pattern with  $J_{AB} \cong 13$  c./s. and  $\Delta\nu \cong 12.5$  c./s. It is quite possible that the crystalline form of peroxide IV exists as a single stereoisomer, presumably the *trans* isomer which becomes equilibrated in solution into a 2:3 mixture of *cis* and *trans* forms as shown by the n.m.r. measurements in  $\text{CDCl}_3$ . The  $\text{CD}_3\text{OD}$  spectrum looks similar, but in  $\text{D}_2\text{O}$  solution the deuteration leads from a  $\text{CH}_2$  to a  $\text{CHD}$  resonance which is broadened by a quadrupolar relaxation of the deuteration.

Neither the infrared nor the n.m.r. spectra show evidence of the presence of peroxide III. If this peroxide is formed either from 2,4-pentanedione and hydrogen peroxide or from the rearrangement of peroxide IV, it must dissociate spontaneously in solution to give hydrogen peroxide and a mixture of the chelated and unchelated 2,4-pentanedione.

The interpretation of the n.m.r. spectra of peroxide V is somewhat uncertain. There is a smaller amount of acetylacetone present in solution than in the case of peroxide IV. Both the  $\text{CD}_3\text{OD}$  and  $\text{D}_2\text{O}$  spectra show a single as well as a slightly broadened methylene resonance. This indicates that it is reasonable to assume that the only isomer present is the *trans* isomer

(16) C. F. W. G. Schneider and L. W. Reeves, *Ann. N. Y. Acad. Sci.*, **70**, 858 (1958).

since for this case the difference in chemical shielding for the two methylene protons is probably small. Throughout there are two strong methyl resonances which are about 6 c./s. apart. An additional methyl resonance goes back to the presence of small amounts of peroxide IV.

Peroxides VI and VII give easily interpretable spectra which consist in two lines of the intensity ratio 2:6. Peroxide VI is the *trans* isomer since there is no AB-pattern for the methyl resonance as observed in the spectrum of peroxide IV. In peroxide VII the methylene protons are magnetically equivalent by reason of the symmetry of the molecule which can exist only in the *cis* configuration.

### Experimental

**3,5-Dimethyl-3,5-dihydroxy-1,2-peroxycyclopentane (IV).**—To 30.0 g. of freshly distilled 2,4-pentanedione (acetylacetone), b.p. 138–139°, free from organic acids and cooled to 0° was added dropwise in the course of 0.5 hr. with frequent shaking 20.40 g. of 50% hydrogen peroxide. The mixture was allowed to stand at 0° with occasional shaking for 4 hr. whereby it crystallized into a solid mass. The solid was separated by filtration and allowed to dry on a porous plate overnight; 57–61°, yield 36.2 g. (90%). This was extracted in a Soxhlet with hot petroleum ether. Only small amounts of impurities were extracted. The remaining solid was recrystallized several times at –10° from either anhydrous ether or dichloromethane; m.p. 90–91°. A paper chromatogram using a modification of the method of Cartledge and Tipper<sup>17</sup> gave a single spot with an  $R_f$  of 0.28.

This peroxide is very soluble in water and is not sensitive to shock. The infrared spectrum of a Nujol mull of this peroxide showed the following bands in  $\text{cm}^{-1}$ ; the numbers in parentheses give the intensity of each band: 3350 (8.6), 2850–2980 (9.7), 1460 (9.1), 1450 (9.1), 1415 (7.6), 1375 (8.9), 1308 (8.4), 1200 (8.8), 1165 (8.8), 1078 (8), 972 (8.1), 918 (6.7), 890 (4.2), 860 (8.5), 825 (7.9), 728 (6.8). The infrared spectrum of this peroxide taken in dimethoxyethane under a high resolution using a calcium fluoride prism showed a strong band at 3560  $\text{cm}^{-1}$ , the intensity of which decreased with dilution. Since dimethoxyethane is an ether this effect was expected.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{10}\text{O}_5$ : C, 44.77; H, 7.51; (O), 11.93; mol. wt., 134.1. Found: C, 44.75; H, 7.32; (O), 12.12 (KI +  $\text{CH}_3\text{COOH}$  method); mol. wt., 140.2 (cryoscopic in dioxane).

**3,5-Dimethyl-3-hydroxy-5-hydroperoxy-1,2-peroxycyclopentane (V).**—To 40.8 g. (0.6 mole) of 50% hydrogen peroxide maintained at 0° was added dropwise with rapid stirring 30 g. of freshly distilled neutral 2,4-pentanedione. Stirring was continued at room temperature for 4 days; then the mixture was extracted with pentane, but no peroxidic product was extractable. The aqueous layer was then extracted with 2 × 50 ml. of ethyl ether; the ether extract washed with saturated solution of ammonium sulfate, dried over magnesium sulfate and the ether removed in vacuum leaving a white crystalline residue which was dissolved in 100 ml. of dichloromethane by refluxing the solution. When the latter was cooled to –10°, 5.13 g. of a colorless crystalline product separated out, m.p. 105° without decomposition. When the original aqueous layer was allowed to evaporate in an open dish and the solid obtained recrystallized from boiling dichloromethane, an additional 11.47 g. of pure peroxide was obtained; total yield 16.6 g. (37%). Like peroxide IV this peroxide was also insoluble in ordinary solvents, so that the mol. wt. was determined in dioxane. A paper chromatogram using the method cited above gave a single spot with an  $R_f$  of 0.23. The infrared spectrum using the mull method in Nujol showed the following bands in  $\text{cm}^{-1}$ : 3450 (8), 3300 (8.5), 2850–2928 (10), 1440–1460 (10), 1370 (9.5), 1300 (8.2), 1275 (6.7), 1150–1170 (9), 1080 (8.5), 1040 (4.5), 960 (8.5), 930 (4.5), 915 (5.3), 890 (7.6); 845 (8.8), 820 (8.4), 800 (8.8). The infrared spectrum in dimethoxyethane using a calcium fluoride prism showed a strong band at 3500  $\text{cm}^{-1}$ , the intensity of which decreased with dilution.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{10}\text{O}_5$  (V): C, 40.01; H, 6.71; (O), 21.31; mol. wt., 150.1. Found: C, 40.1; H, 6.68; (O), 21.31; mol. wt., 148 (cryoscopic in dioxane).

Peroxide V is very sensitive to shock; it is stable indefinitely at 50° but decomposes slowly at 70° with evolution of oxygen. Attempts to prepare the *p*-nitrobenzoate derivative were not successful. Peroxide V was also prepared in somewhat higher yields by allowing peroxide IV to react in water solution at 0° with one mole equivalent of hydrogen peroxide. A yield of 75%

was obtained; m.p. 105° (dichloromethane), and mixed m.p. with V showed no depression.

**3,5-Dimethyl-3,5-Dihydroperoxy-1,2-Peroxcyclopentane (VI).**—To a mixture of 109 g. (1.6 moles) of 50% hydrogen peroxide and 1.4 g. of sulfuric acid maintained at 0° was added dropwise in the course of 0.75 hr. with rapid stirring 50 g. (0.5 mole) of pure 2,4-pentanedione. The mixture was allowed to stand at 0° overnight, then extracted with 3 × 300 ml. of pure ether and the ether extracts shaken for several hours with about 15 g. of magnesium carbonate containing 40% magnesium oxide. Finally, the ether was dried over magnesium sulfate, filtered and the ether removed under reduced pressure. A white solid residue remained; yield 75 g. This was recrystallized several times from hot dichloromethane and the fractions (63% of the original) which crystallized in large plates at room temperature had a m.p. of 108° (without decomposition). This peroxide is extremely sensitive to shock and explodes with considerable brisance. A paper chromatogram prepared by the method of Cartledge and Tipper<sup>17</sup> showed a single spot with an  $R_f$  of 0.33. The infrared spectrum using the mull method showed the following bands in  $\text{cm}^{-1}$ : 3350 (7), 2900 (9.7), 1460–1450 (9.4), 1370 (9.1), 1330 (6.4), 1225 (5.7), 1165 (7.4), 1090 (6.1), 950 (5.1), 918 (4.9), 890 (5.3), 845 (5.9), 810 (4.5), 785 (5.8), 720 (4.1). The infrared spectrum in dimethoxyethane using a calcium fluoride prism showed a strong band at 3450  $\text{cm}^{-1}$ , the intensity of which decreased with dilution.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{10}\text{O}_6$ : C, 36.16; H, 6.07; (O), 28.9; mol. wt., 166.1. Found: C, 36.38; H, 6.22; (O), 29.1 (HI +  $\text{CH}_3\text{COOH}$  method), 28.9 (KI +  $\text{CH}_3\text{COOH}$  method); mol. wt., 174.5 (cryoscopic in dioxane).

**Bis-*p*-nitrobenzoate of VI.**—This derivative was prepared by the method of Brewster and Cotte.<sup>18</sup> To 20 ml. of dry pyridine maintained at 0° was added 2.1 g. of *p*-nitrobenzoic acid and 4.3 g. of benzenesulfonyl chloride followed by 1.0 g. of peroxide VI. The mixture was allowed to stand at 0° for 2 hr., then poured on ice and the solid which separated collected and dried in air; yield 2.0 g. (71%). This derivative was recrystallized from hot absolute ethyl alcohol; m.p. 175° dec.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_{12}$ : C, 49.14; H, 3.47; N, 6.04; (O), 10.34. Found: C, 49.42; H, 3.53; N, 5.94; (O), 10.36 (NaI +  $\text{CH}_3\text{COOH}$  +  $\text{Fe}^{+++}$ ).<sup>19</sup>

From the mother liquors was also isolated in small amounts a volatile peroxide, m.p. 125–126°, which was identical with peroxide VII.

**3,5-Dimethyl-3,5-dihydroperoxy-1,2-peroxycyclopentane (VI). Alternate Method.**—To 13.4 g. (0.1 mole) of peroxide IV maintained at 0° was added dropwise with vigorous shaking in the course of 0.5 hr. 13.6 g. of 50% hydrogen peroxide containing 1% sulfuric acid. The mixture was allowed to stand at 0° for 1 hr., then at room temperature for 24 hr. It was then extracted with 2 × 100 ml. of ether and the ether solution shaken with about 0.2 g. of magnesium carbonate containing 40% magnesium oxide, dried with magnesium sulfate and the ether removed in vacuum; yield of crude solid, 16.5 g. (98%). This was recrystallized from dichloromethane into colorless plates, m.p. 108°, and was found to be identical with peroxide VI.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{10}\text{O}_6$ : (O), 28.90. Found: (O), 28.85 (HI +  $\text{CH}_3\text{COOH}$  method).

**Preparation of Peroxide VII.**—To 100 mg. of peroxide V dissolved in 100 ml. of anhydrous ether and the solution cooled to 0° was added with frequent shaking 2 g. of phosphorus pentoxide in eight equal portions during 8 hr. The mixture was then filtered into a separatory funnel and the ether solution washed successively each with 50 ml. of saturated solution of sodium bicarbonate and water, dried over magnesium sulfate, filtered and the filtrate concentrated in vacuum to one fourth its original volume. When the solution was cooled to –10° long, colorless needles crystallized (50% yield) which were recrystallized from ether; m.p. 125–126°. A paper chromatogram using Whatman paper No. 1 impregnated with dimethylformamide and developed with decalin saturated with dimethylformamide gave a single spot when sprayed with a mixture of hydrogen iodide and glacial acetic acid with an  $R_f$  of 0.083. This peroxide is very volatile and the chromatogram should be sprayed immediately after development. A chromatogram prepared according to the method of Cartledge and Tipper<sup>17</sup> gave an  $R_f$  of 0.71. This peroxide is also sensitive to shock and explodes with considerable brisance. The infrared spectrum 10% in chloroform showed the following principal bands in  $\text{cm}^{-1}$ : 3000 (5.5), 2980 (2.5), 1440 (6), 1435 (8.5), 1375 (9.5), 132–(9.5), 1230–1210 (4.5), 1190 (9), 1175–1165 (9.7), 990 (3), 925 (4), 870 (8), 840 (9.7).

*Anal.* Calcd. for  $\text{C}_8\text{H}_8\text{O}_4$ : C, 45.44; H, 6.10; (O) 24.2; mol. wt., 132. Found: C, 45.26; H, 5.97; (O) 24.2 (HI +  $\text{CH}_3\text{COOH}$  method); mol. wt., 133 (cryoscopic in dioxane).

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

(19) L. S. Sibert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

(17) J. Cartledge and C. F. H. Tipper, *Anal. Chem. Acta*, **22**, 106 (1960).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE, NEWARK, DEL.]

### Mechanisms of Acid-catalyzed Reactions. III. Oxotropic Rearrangement of $\alpha$ -Phenylallyl Alcohols

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The solvent composition–acidity function criterion<sup>1a,c</sup> and the Bunnett<sup>1b</sup> H<sub>2</sub>O activity relation have been simultaneously applied as probes of the mechanism of oxotropic rearrangement of  $\alpha$ -phenylallyl alcohols in hydroxylic solvents. The results obtained appear to describe a transition state which does not involve the nucleophilic properties of water and appears to contradict earlier interpretations<sup>5,6,11</sup> of the course of reaction.

The structure of the carbonium ion intermediate in anionotropic rearrangements of uncharged allylic derivatives in non-aqueous systems has been examined in considerable detail.<sup>2</sup> Though current knowledge of the nature of the ion pairs that develop with ionization

of the  $\text{—C—X}$  bond is indeed very extensive, compara-

tively little is known about the oxotropic reaction of cationic allylic substrates in aqueous or partly aqueous systems. That is to say, the formation of carbonium ion-pair intermediates are commonly conceded to form in the solvolysis of *uncharged* phenylallyl derivatives,<sup>2,3</sup> although some covalent character in the transition state bonding has been invoked on occasion to explain certain features of this reaction.<sup>4</sup> There exists, however, considerable disagreement as to the course of reaction and nature of the intermediates in the solvolysis of the (charged) conjugate acids of phenylallyl alcohols, the so-called oxotropic rearrangement.

Thus, Braude, Jones and Stern<sup>5</sup> have investigated the rearrangement of phenylpropenylcarbinol by determining the reaction rate as a function of medium over a wide range of ethanol–water solvent compositions. These authors applied as a kinetic criterion of mechanism a proposed medium dependence of isodielectric energy of activation<sup>5,6</sup> and other criteria which led them to suggest the intramolecular or S<sub>2</sub>' processes discussed by Braude in a series of review articles.<sup>7</sup> The rearrangement of the simpler homolog phenylvinylcarbinol to cinnamyl alcohol could not be incorporated into the study since in ethanol–water solutions this substrate is partially etherified *via* displacement<sup>8</sup> before the rearrangement step and the ether rearranges in acid at a slower rate. However, by extrapolation of their conclusions regarding phenylpropenylcarbinol it was suggested that phenylvinylcarbinol also rearranges *via* A<sub>2</sub>.

Subsequently, workers in the British laboratory<sup>8,9</sup> studying the solvolysis of 1-phenylallyl chloride in

aqueous dioxan and aqueous alcohol solutions inferred that a limiting S<sub>N</sub>1 mechanism did obtain in this system as judged from its (determined) *m*-value of the Grunwald–Winstein relationship.<sup>10,11</sup> But, surprisingly, nearly all of the solvolytic product was the 1-phenylallyl derivative (ether or alcohol), leading the authors to conclude that a “hot” carbonium ion<sup>12</sup> (reacting with solvent before it could be delocalized) was to be preferred. These results with the *uncharged* phenylallyl derivative, however, were distinctively different from those obtained through solvolysis of phenylallyl oxonium ion in aqueous dioxane (60:40, v./v.) by Bunton, Pocker and Dahn.<sup>13</sup> They observed by use of H<sub>2</sub>O<sup>18</sup> tagging that the over-all rate of formation of carbonium ions was about 2.5 times greater than the rate of rearrangement. Furthermore, the occurrence of an A<sub>1</sub> reaction process was identified by the linear relation (slope = 1.3) between the Hammett acidity function *H*<sub>0</sub> and the rate in the dioxane–water medium. They have interpreted these data to be in contradiction with the intramolecular and S<sub>2</sub>' processes of oxotropic rearrangement proposed by Braude<sup>7</sup> as represented in Fig. 1 by paths a and/or b.

Goering and Dilgren<sup>14</sup> have conducted some very elegant studies of the racemization, O<sup>18</sup> exchange and rearrangement reactions taking place with optically active  $\alpha$ -phenylallyl alcohol in aqueous acid–dioxane media. Their results serve to elaborate the earlier work<sup>13</sup> by demonstrating that the rates of racemization are greater than the rates of O<sup>18</sup> exchange, which, in turn, are greater than the rates of rearrangement.

Goering<sup>14b</sup> has considered two possible mechanisms that are consistent with these data. The one chosen as the more likely is (the A<sub>1</sub>) represented by path f (see Fig. 1). The alternative may be described as a combination of S<sub>N</sub>2 and S<sub>N</sub>2' displacement that are equivalent to a tandem of path d followed by path b and/or path c. In the final analysis, however, their preference for path f is based on the reported<sup>7</sup> adherence of the rate (in aqueous ethanol solution) to an *H*<sub>0</sub> dependence.

Others have disputed the latter argument, regarding the *H*<sub>0</sub> criterion as dubious evidence for the choice of path f. It is particularly difficult to ignore the valid objection raised by Gutbzahl and Grunwald<sup>15</sup> con-

(1) For previous papers in this series see: (a) H. Kwart and L. B. Weisfeld, *J. Am. Chem. Soc.*, **80**, 4670 (1958); (b) H. Kwart and A. L. Goodman, *ibid.*, **82**, 1947 (1960); (c) H. Kwart and M. B. Price, *ibid.*, **82**, 5123 (1960).

(2) See H. L. Goering, *Rec. Chem. Progr.*, **21**, 109 (1960), for a thorough review of this subject.

(3) In addition to the work so excellently summarized in ref. 2 see also: (a) R. A. Sneen, *J. Am. Chem. Soc.*, **82**, 4261 (1960); (b) R. A. Sneen and A. M. Rosenberg, *ibid.*, **83**, 895, 900 (1961).

(4) H. L. Goering, *et al.*, *ibid.*, **77**, 1129, 5026, 6249 (1955).

(5) E. A. Braude, E. R. Jones and E. S. Stern, *J. Chem. Soc.*, 396 (1946).

(6) E. A. Braude, *ibid.*, 443 (1944).

(7) E. A. Braude, *Ann. Reports*, **46**, 125 (1949); *Quart. Revs.*, **4**, 404 (1950).

(8) E. A. Braude, G. Wolkanas and E. S. Waight, *Chemistry & Industry*, 314 (1956).

(9) G. Wolkanas and E. S. Waight, *Proc. Chem. Soc.*, 8 (1959).

(10) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(11) A. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(12) D. Semenov, Chin-Hua Shih and W. G. Young, *ibid.*, **80**, 5472 (1960).

(13) C. A. Bunton, Y. Pocker and H. Dahn, *Chemistry & Industry*, 1516 (1958).

(14) (a) H. L. Goering and R. E. Dilgren, *J. Am. Chem. Soc.*, **81**, 2556 (1959); (b) **82**, 5744 (1960).

(15) B. Gutbzahl and E. Grunwald, *ibid.*, **75**, 559 (1953).