1,4-butanedisulfonate, 25056-40-0; ethyl 1-nitro-1-butanesulfonate, 25056-42-2; neopentyl 1-bromo-1-nitroethanesulfonate, 25056-43-3; neopentyl 1-bromo-1-nitrobutanesulfonate, 25056-44-4; ethyl 1-bromo-1-nitrobutanesulfonate, 25056-45-5; dineopentyl 1,4-dibromo-1,4-dinitro-1,4-butanedisulfonate, 25056-46-6; neopentyl 1-bromo-1-nitrohexanesulfonate, 25056-47-7.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work.

Formation, Proof of Structure, and Thermal Decomposition of Peroxide from Benzyl Mesityl Ketone[1]

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Experimental conditions for autoxidation of benzyl mesityl ketone to a peroxide were investigated. The peroxide was characterized as 2-hydroperoxy-2-phenyl-2′,4′,6′-trimethylacetophenone (III) by ir and ^{1}H nmr spectra, and iodide reduction to the known 2,4,6-trimethylbenzoin (IV). Solid-state thermal decomposition of III forms mesitoic acid and benzaldehyde in equal amounts by one pathway and mesityl phenyl diketone (V) and water by another. The latter is a new mode of thermal decomposition for α-keto hydroperoxides. Decomposition also takes place slowly by both pathways at room temperature on standing in contact with a glass surface. Differential thermal analysis and differential scanning calorimetry studies under various conditions show that decomposition of III occurs in the solid phase without prior melting. A mechanism is proposed for the two modes of decomposition.

In a previous paper[4] on the autoxidative cleavage of isopropyl mesityl ketone to mesitoic acid and acetone,[5] an intermediate peroxide was detected but could not be isolated for characterization. A study of time sequential infrared spectra of oxidation mixtures indicated the α-keto hydroperoxide structure (Ia) in preference to an isomeric oxaoxetane formulation (Ib) (Scheme I). Kohler who was the first to report[6] a stable keto peroxide formulated structures analogous to Ib.[7] Rigaudy observed[8] ultraviolet absorption in the carbonyl region for Kohler's keto peroxides and formulated their structures as keto hydroperoxides analogous to Ia; carbonyl bands in the infrared spectra were reported by Fuson and Jackson[9] in confirmation of Rigaudy's formulation. The present paper reports the formation, characterization by infrared and ^{1}H nmr spectra and chemical methods, and thermal decomposition of a stable peroxide isolated from autoxidation of benzyl mesityl ketone (II)[10] which was originally prepared for use in studies of structures of Grignard compounds derived from hindered ketones.[13]

Results and Discussion

Autoxidation.—The samples of benzyl mesityl ketone (II) were obtained as liquids[14] which solidified or precipitated peroxides after standing in stoppered or unstoppered vessels for varying lengths of time (15 days to 6 months). A number of qualitative observations were made on autoxidative behavior of II in order to ascertain conditions under which oxidation could be accelerated or minimized. The random nature of the autoxidations was evident from 15 experiments[15] which were carried out. The following observations can be made. Autoxidation proceeded as readily (1) when apparatus was flushed with nitrogen as when allowed to stand in contact with air, (2) when oxygen was bubbled through the liquid or a solution or allowed to stand, and (3) whether exposed to light or shielded from it. Traces of oxygen appeared to be sufficient to result in autoxidation. In one experiment no peroxide precipitate was observed[16] when the sample was allowed to stand undisturbed exposed to air for 11 months. The recommended procedure for conducting the autoxidation is simply to allow the liquid ketone to stand in a vessel with maximum surface area exposed to the atmosphere and to agitate the sample occasionally. The best conditions found for minimizing autoxidation of II were to carry out preparation and handling of the compound in a rigorously deoxygenated nitrogen atmosphere and to store the compound at low temperature.

Spectral and Chemical Proof of Structure of Peroxide III.—Ir and ^{1}H nmr spectra are consistent with an α-keto hydroperoxide structure (III). The ir spectrum

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[1] A. G. Pinkus, M. Z. Haq, and J. G. Lindberg, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, ORGN-59.

[2] Robert A. Welch Foundation postdoctoral fellow.

[3] Robert A. Welch Foundation predoctoral fellow.

[4] A. G. Pinkus, W. C. Servoss, and K. K. Lum, *J. Org. Chem.*, **32**, 2649 (1967).

[5] Water was also found to be a product.

[6] E. P. Kohler, *Amer. Chem. J.* **36**, 177, 529 (1906).

[7] E. P. Kohler and R. B. Thompson, *J. Amer. Chem. Soc.*, **59**, 887 (1937).

[8] J. Rigaudy, *C. R. Acad. Sci., Paris*, **226**, 1993 (1948)

[9] R. C. Fuson and H. L. Jackson, *J. Amer. Chem. Soc.*, **72**, 1637 (1950).

[10] Two recent papers on α-keto hydroperoxides have appeared. One paper[11] mainly concerned with hydrogen-bonding aspects of two keto hydroperoxides was published when the present work was well under way. When this paper appeared we discontinued our ir and ^{1}H nmr studies on hydrogen bonding of the hydroperoxides but completed other aspects of the problem. A second paper[12] which appeared after the present work was complete, deals with preparation and properties of aliphatic α-keto hydroperoxides.

[11] W. H. Richardson and R. F. Steed, *J. Org. Chem.*, **32**, 771 (1967).

[12] R. C. P. Cubbon and C. Hewlett, *J. Chem. Soc., C*, 2978 (1968).

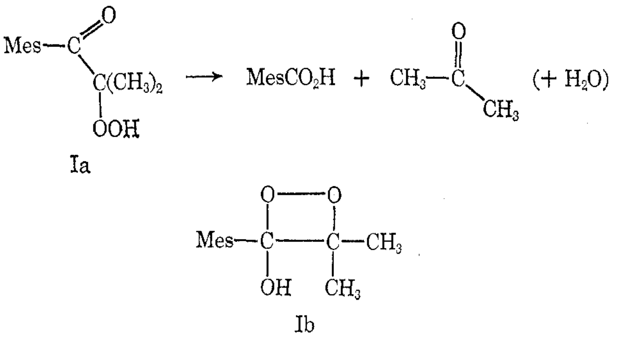
[13] A. G. Pinkus, J. G. Lindberg, and A. B. Wu, *ibid.*, *D*, 1351 (1969).

[14] H. H. Weinstock, Jr., and R. C. Fuson, *J. Amer. Chem. Soc.*, **58**, 1233 (1936), report mp 32.0–32.5°.

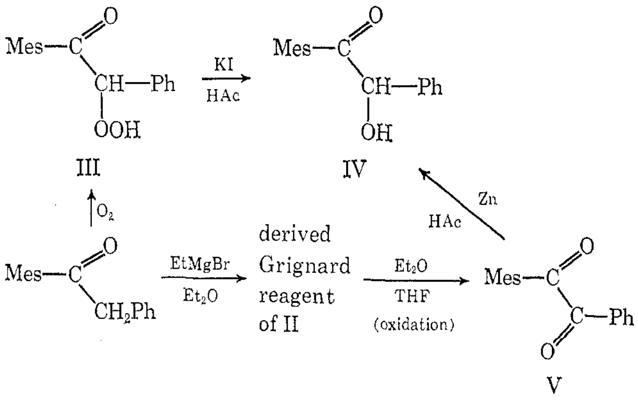
[15] A table summarizing the results of these experiments was eliminated from the original paper to save space.

[16] An ir spectrum of the mother liquor from one of the experiments showed no detectable amount of peroxide; this would indicate solubility of peroxide to be low in this mixture. Although peroxide was not tested for in this sample, it is possible that it could have been present in solution in small amount.

SCHEME I



SCHEME II



of III showed a carbonyl stretching band, an -O-O- band, and O-H stretching bands (for -OOH). Similar carbonyl and -OO-H stretching bands were observed in the present investigation for 3,3-diphenyl-2-hydroperoxy-2′,4′,6′-trimethylpropiophenone[17] (one of "Kohler's peroxides").

The ^1H nmr spectrum[19] of III showed a singlet at 9.62 ppm for the OOH proton. (Other chemical shifts are in the Experimental Section.) Hydroperoxy protons show characteristic low-field absorption[20] indicating considerable deshielding. For the only previously reported ^1H nmr absorption for an α-keto hydroperoxide, Richardson and Steed[11] listed 9.39 ppm for the hydroperoxy proton of 2,4-dimethyl-2-hydroperoxy-3-pentanone. The corresponding signal for 3,3-diphenyl-2-hydroperoxy-2′,4′,6′-trimethylpropiophenone observed in the present work was at 9.28 ppm.

III gave a positive iodide test for active oxygen. A quantitative determination using an iodometric titration method[21] showed one active oxygen per molecule of III. For a chemical proof of structure, hydroperoxide III on reduction with potassium iodide was converted into 2,4,6-trimethylbenzoin (IV); the latter was previously prepared by Fuson and coworkers by zinc-acetic acid reduction of mesityl phenyl diketone (V)[14] (Scheme II) and aluminum chloride catalyzed condensation of mesitylglyoxal and benzene.[22]

Thermal Decomposition of 2-Hydroperoxy-2-phenyl-2′,4′,6′-trimethylacetophenone (III).—On heating in a flame, III decomposed explosively. Under milder conditions[23] the following products of decomposition were isolated and characterized: mesitoic acid, benzaldehyde, mesityl phenyl diketone (V),[24] and water. Quantitative determinations of the amounts of products showed that mesitoic acid (49% average yield) and benzaldehyde were formed in equivalent amounts; this fact is important in the consideration of a mechanism for the decomposition. This result contrasts with that reported previously[4] for the autoxidative cleavage of isopropyl mesityl ketone where the molar quantity of acetone exceeded that of mesitoic acid (ratio of $0.709:0.478 = 1.48$).[25] Because of experimental difficulties it was not possible to determine the amount of water quantitatively in the present investigation.

α-Keto hydroperoxides are reported[26] to decompose thermally to carboxylic acids and aldehydes or ketones. The present investigation shows that an additional mode of thermal decomposition to an α,β diketone and water can occur simultaneously. The two different pathways are summarized in Scheme III. The total overall yield for the two pathways (average of three experiments) was 60%.[27]

Decomposition was also studied by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). It was of particular interest to ascertain by these techniques whether or not the hydroperoxide melted and then decomposed, or whether direct decomposition of the solid took place. In previous reports[6,7,9,28] keto hydroperoxides have been stated to decompose at or slightly above their melting points. The two alternatives should be readily distinguishable by DTA or DSC since prior melting followed by decomposition would be expected to produce two peaks, one endothermic owing to melting followed closely by an exothermic decomposition peak, whereas only a single peak (probably exothermic)[29] would be expected for direct decomposition of solid hydroperoxide. Only a single[30] sharp exothermic peak was observed using both

[17] Originally prepared by Kohler, *et al.*;[6,7,18] ir and ^1H nmr spectra first obtained and reported in the present work.

[18] E. P. Kohler and C. E. Barnes, *J. Amer. Chem. Soc.*, **55**, 690 (1933); E. P. Kohler, M. Tishler, and H. Potter, *ibid.*, **57**, 2517 (1935).

[19] ^1H nmr spectra for III and the "Kohler peroxide" are the first to be reported for aromatic keto hydroperoxides; the only previous complete ^1H nmr spectrum given for a keto hydroperoxide was for an aliphatic derivative.[11]

[20] S. Fujiwara, M. Katayama, and S. Kamio, *Bull. Chem. Soc. Jap.*, **32**, 657 (1959); D. Swern, A. H. Clements, and T. M. Luong, *Anal. Chem.*, **41**, 412 (1969).

[21] M. V. Goftman and G. D. Kharlampovich, *J. Appl. Chem. USSR*, **30**, 465 (1957) [*Zh. Prikl. Khim.*, **30**, 439 (1957)].

[22] R. C. Fuson, H. H. Weinstock, Jr., and G. E. Ullyot, *J. Amer. Chem. Soc.*, **57**, 1803 (1935).

[23] Controlled heating in air, *in vacuo* under nitrogen, or at atmospheric pressure; the same products were found under these varied conditions. Decomposition on a vpc column at 200° was also studied; the peak for benzaldehyde was identified conclusively.

[24] Mesityl phenyl diketone (V) was also obtained in the present work in 7.9% yield during an attempted preparation of the enol ether of benzyl mesityl ketone (II) by methylation of the derived bromo Grignard reagent of II, oxidation having taken place.

[25] A tentative explanation for deviation from the expected 1:1 ratio has been presented.[4]

[26] Earlier work is reviewed by E. G. E. Hawkins, "Organic Peroxides," Van Nostrand, Princeton, N. J., 1961, pp 116, 381 ff; L. Horner, "Autoxidation and Antioxidants," Vol. I, W. O. Lundberg, Ed., Interscience, New York, N. Y., 1961, Chapter 5; A. G. Davies, "Organic Peroxides," Butterworths, London, 1961.

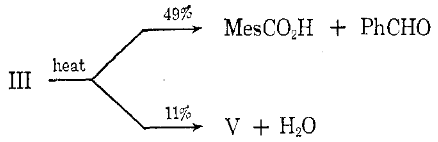
[27] An unidentified residue accounted for the remaining 40% from decomposition of III after separation and analysis of products as described. Several preliminary experiments were carried out to establish optimum conditions for decomposition.

[28] R. C. Fuson, E. W. Maynert, and W. J. Shenk, Jr., *J. Amer. Chem. Soc.*, **67**, 1939 (1945).

[29] This would depend on the relative magnitude of the enthalpy of decomposition compared with that of fusion.

[30] Other peaks appeared at much higher temperatures owing to vaporization and possible further decomposition of products of initial decomposition. During observations taken while obtaining the melting point of III, the material in the capillary after decomposition was liquid. Furthermore, DTA and DSC curves did not show any peaks corresponding to melting points of mesitoic acid and mesityl phenyl diketone, indicating that these were in a molten state.

SCHEME III

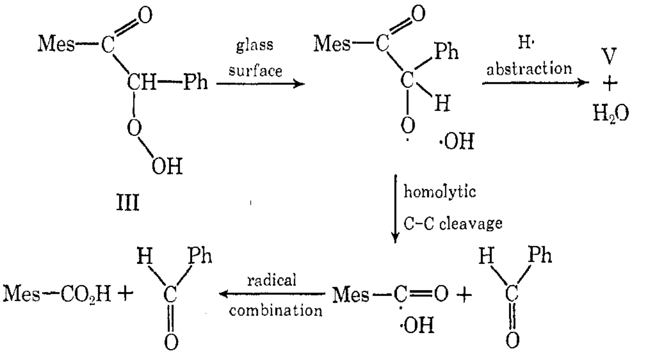


DSC and DTA under all conditions studied showing that the solid decomposed directly without first melting. Temperatures of decomposition (average) were 135° with DTA and 139.8° with DSC.

Stability of Hydroperoxide (III).—Freshly prepared samples of III having a white crystalline appearance slowly turned yellow[31] after standing at room temperature in stoppered glass containers whether kept in the dark or exposed to ordinary daylight. The odor of benzaldehyde was also evident. These observations show that both modes observed for thermal decomposition are also operative for slow room temperature decomposition. An interesting aspect of the decomposition was that only material in contact with the glass container turned yellow in samples examined; material in the interior of the sample or on top was unchanged.[32] Evidently decomposition is catalyzed by contact with the glass surface.[33] Freshly prepared samples of peroxide III showed no detectable[36] decomposition after standing in stoppered vials for nearly two years in a refrigerator.

Mechanism of Thermal Decomposition.—Mechanisms of thermal decompositions of alkyl hydroperoxides have been extensively investigated[26,35,37] although much less work has been done on α-keto hydroperoxides. The following proposed tentative mechanism[38] (Scheme IV) for solid-state thermal decomposition of III is adapted from mechanisms for other hydroperoxide decompositions.[35,37] The initiation step is postulated as cleavage of the O–O bond. Although Benson[39] showed that homolysis of the peroxide bond contributed negligibly to kinetics of decomposition of *t*-butyl hydroperoxide *in solution*, adsorption on the glass wall surface in the case of the *solid* keto hydroperoxide at the peroxy oxygens could result in a lowering of the energy of activation in the latter case. The second step could take place in two ways. Abstraction of the α-hydrogen atom by hydroxyl radical would form mesityl phenyl diketone and water. In the other pathway, homolytic cleavage of the carbon–carbon bond would give benzaldehyde and mesitoyl radical; in a radical combination step the latter would react with hydroxyl radical to form mesitoic acid. These pathways account for *ca.* 60% of the products. The remaining 40% of products could be formed by other reactions of the two radicals formed in the first step. Since mesitoic acid and benzaldehyde are formed in nearly equal amounts, it is unlikely that the mesitoyl radical undergoes any reaction other than combination with hydroxyl to form mesitoic acid. Thus, the remaining products must be formed at some other stage of the reaction or by some other pathway. Although 2,4,6-trimethylbenzoin (IV) would be expected to be formed by abstraction of a proton by the initial cleavage fragment (other than hydroxyl), the ir spectrum of the residue showed a carbonyl band only at 1818 cm^{-1}, whereas IV has this band at 1685 cm^{-1}; this shows the absence of IV.

SCHEME IV



Experimental Section[40]

Benzyl Mesityl Ketone (II).—II was prepared in 68–79% yield by Friedel-Crafts reaction[41] of mesitylene and phenylacetyl chloride in petroleum ether (bp 65–110°) using aluminum chloride and also by polyphosphoric acid[42] catalyzed condensation[43] of mesitylene and phenylacetic acid in 56.5% yield. The product was distilled under nitrogen: bp 160–165° (<1 mm); ir[44] (neat) 1682 cm^{-1} (C=O); ^1H nmr[45] (CCl_4) 7.14 (5, C_6H_5), 6.69 (2, Mes-H_2), 3.82 (2, CH_2), 2.18 (3, *p*-CH_3), 1.99 (6, *o*-CH_3).

Autoxidation of Benzyl Mesityl Ketone (II) to 2-Hydroperoxy-2-phenyl-2′,4′,6′-trimethylacetophenone (III).—II on standing in various containers at room temperature autoxidized to III. The time period for autoxidation of II and the yields of III varied from 7 to 8% (for those determined) depending on conditions;

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[31] The change was noticeable after 3–4 months; in a separate experiment the yellow substance was identified as mesityl phenyl diketone (V) by means of thin layer chromatography.

[32] This observation suggests the possibility that decomposition at room temperature might be prevented or slowed in other types of containers made of plastic, *etc.*; however, this was not investigated. Conversely, in the cases studied, thermal decomposition is evidently initiated on the glass or metal surface (spatula, DSC and DTA surfaces).

[33] A difference in rates of decomposition of *t*-butyl hydroperoxide in solution was noted by Bulygin and Zaikov[34] for glass and metallic reactors. They attributed the change in rate to the nature of the reactor wall. Hiatt and Irwin[35] reported that the first-order rate constant for decomposition of a solution of *t*-butyl hydroperoxide was increased by 60% when the surface to volume ratio was increased sevenfold by using crushed Pyrex tubing.

[34] M. G. Bulygin and G. E. Zaikov, *Bull. Acad. Sci. USSR*, 481 (1968) [*Izv. Akad. Nauk SSSR*, 491 (1968)].

[35] R. Hiatt and K. C. Irwin, *J. Org. Chem.*, **33**, 1436 (1968).

[36] No benzaldehyde odor, yellow color formation, or melting point change.

[37] The recent series of papers by R. Hiatt and coworkers summarize the current state of knowledge in this area: R. Hiatt, T. Mill, and F. R. Mayo, *J. Org. Chem.*, **33**, 1416 (1968); R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *ibid.*, 1421, 1428, (1968); R. Hiatt, K. C. Irwin, and C. W. Gould, *ibid.*, 1430 (1968); ref 35. The paper by Bulygin and Zaikov[34] is a leading reference to recent Russian work in this area.

[38] The editor suggested another possible mechanism for formation of acid and aldehyde by intramolecular reaction of the oxygen of the peroxygen linkage with the carbonyl carbon of III which would afford a species which could decompose directly to acid and aldehyde. Another possible mechanism previously considered was addition of the hydroperoxy proton and oxygen across the carbonyl to form an intermediate analogous to Ib which could then undergo fragmentation to form acid and aldehyde by one pathway and diketone and water by another.

[39] S. W. Benson, *J. Chem. Phys.*, **40**, 1007 (1964).

[40] Melting points are corrected; boiling points are uncorrected.

[41] A. Klages and G. Lickroth, *Chem. Ber.*, **32**, 1549 (1899).

[42] The authors thank FMC Corp. for a sample of 115% polyphosphoric acid.

[43] Conditions for the preparation were determined from reactions described in reviews on polyphosphoric acid condensations: F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958); F. Uhlig and H. R. Snyder in "Advances in Organic Chemistry, Methods and Results," R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Vol. I, Interscience, New York, N. Y., 1960, pp 35–81.

[44] Frequencies in cm^{-1}; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad, sp = sharp.

[45] δ in parts per million from tetramethylsilane as internal reference; s = singlet, br = broad, m = multiplet; relative peak areas in parentheses.

optimum procedure was to allow II to stand with maximum surface area exposed to air with occasional agitation. Two analytical samples were prepared. The first sample[46] was recrystallized from carbon tetrachloride and then from *n*-hexane, mp[47] 125.5–126.2° dec. The second sample[48] after washing with several portions of *n*-hexane melted[47] at 130–132° dec. After two recrystallizations from ethyl acetate, III had mp[47] 134–135° dec. *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.54,[46,49] 75.65[48,50]; H, 6.64,[46,49] 6.78.[48,50] The following spectral data were obtained: ir[44] 1680 (CH_2Cl_2), 1698 (Nujol) (C=O), 888 (Nujol) (–O-O–), 3470[51] (intramolecularly bonded OH), 3330 (CH_2Cl_2) (sh) (intermolecularly bonded OH). Only the 3330 cm^{-1} band appeared for the solid (Nujol mull). ^{1}H nmr[45] (CCl_3Br and $CDCl_3$ solvents, respectively, for each data set reported): 9.36 (1), 9.62 (OO**H**); 7.08 (5), 7.28 ($C_6\mathbf{H}_5$); 6.54 (2), 6.74 (Mes-$\mathbf{H}_2$); 5.72 (1), 5.99 [C**H**(Ph)OO]; 2.19 (3), 2.22 (*p*-C$\mathbf{H}_3$); 1.86 (6), 1.91 (*o*-C$\mathbf{H}_3$).

Preparation of 3,3-Diphenyl-2-hydroperoxy-2′,4′,6′-trimethylpropiophenone.—Benzalacetomesitylene, mp 61° [52] (recrystallized from petroleum ether, bp 30–60°), was prepared in 94% yield by base-catalyzed condensation of acetomesitylene and freshly distilled benzaldehyde by the method of Kohler and Barnes.[18] *β,β*-Diphenylethyl mesityl ketone, mp[53] 82–83° (from carbon tetrachloride, then absolute ethanol), was prepared by 1,4 addition of phenylmagnesium bromide to benzalacetomesitylene; ir 1685 cm^{-1} (C=O). The peroxide was prepared by oxidation of the enolate of the ketone following the procedure of Kohler and Thompson:[7] 62.5% yield; mp 100–101° (from *n*-hexane);[54] ir[44] 3470[51] (CH_2Cl_2), 3509 (CCl_4),[55] 3410 (sh) (Nujol) (OOH) (intramolecular), 3360 (sh) (CH_2Cl_2), 3390 (Nujol) (OOH) (intermolecular), 1704 (CCl_4)[55] (C=O); ^{1}H nmr[45] (CCl_3CN solvent except where noted) 9.31 (br,[56] 1), 9.28 (CCl_4)[55] (OO**H**), 7.17 (br, 10, $C_6\mathbf{H}_5$), 6.70 (s, 2, Mes-$\mathbf{H}_2$), 4.53 (C**H**Ph_2),[57] 4.75 [C**H**(Ph)OO–],[57] 2.33 (s, 3, *p*-C$\mathbf{H}_3$), 1.88 (s, 6, *o*-C$\mathbf{H}_3$).

Reduction of Hydroperoxide III to 2,4,6-Trimethylbenzoin (IV).—A solution of III (0.2025 g, 7.500×10^{-4} mol) in glacial acetic acid (15 ml) was added dropwise over a 15-min period to a stirred solution of potassium iodide (0.500 g, 3.01×10^{-3} mol) in glacial acetic acid (20 ml). The reaction mixture became dark brown owing to liberated iodine. A solution of sodium thiosulfate (*ca.* 0.1 *N*) was added to the reaction mixture until the latter became colorless. The contents were extracted with several 25-ml portions of ether. Combined ether extracts were washed with dilute sodium hydroxide solution and water several times. The ether solution was dried with anhydrous sodium sulfate. On evaporation of ether, 2,4,6-trimethylbenzoin (IV) (0.182 g, 90% yield) was obtained. After recrystallization from ethanol, IV melted at 100–101° (lit.[22] 102°): ir (CH_2Cl_2) 3445 (sp, OH), 1685 cm^{-1} (C=O).

Thermal Decomposition of 2-Hydroperoxy-2-phenyl-2′,4′,6′-trimethylacetophenone (III). Separation and Characteristics of Products.—Crystalline III on heating at 100–110° (oil bath temperature, 1 mm) for 1.5 hr turned yellow. On prolonged heating (6 hr), a sublimate (see below) consisting of mixed yellow and white crystals was obtained; a distillate (colorless droplets) was also collected in a liquid air trap. The inhomogeneous distillate had a bitter almond-like odor characteristic of benzaldehyde. Anhydrous copper sulfate sprinkled on the distillate turned blue instantaneously indicating the presence of water. The ir spectrum (neat) of the distillate (after drying with anhydrous sodium sulfate) showed the same bands as a spectrum of authentic benzaldehyde.

A dilute solution of sodium hydroxide was added to the sublimate of white and yellow crystals from above. The white portion of sublimate dissolved. The yellow insoluble portion was dissolved in ether and the two layers were separated. When the alkaline solution was acidified with dilute hydrochloric acid a white precipitate formed which was collected by filtration and washed with water. After sublimation at 115–120° (oil bath temperature, 1 mm), the crystals had mp 154–155°.[59] The melting point of the mixture of mesitoic acid from the sublimate and an authentic sample was undepressed. The material on thin layer chromatography[60] showed only one spot, R_f 0.32 (*via* uv light) which had the same mobility as that of an authentic sample of mesitoic acid. A comparison of the ir spectrum of the sample with that of authentic material also confirmed the identity of the sublimate as mesitoic acid.

The yellow ether solution from above was washed with water, dried over anhydrous sodium sulfate, and filtered. On removal of ether with a rotary evaporator, yellow crystals were obtained. After recrystallization from petroleum ether (bp 30–60°), the material melted at 136–137°. The compound showed one tlc[60] spot (R_f 0.73); the R_f value corresponded with that from an authentic sample of mesityl phenyl diketone (V). The ir[44] spectrum[61] (Nujol) of V showed absorption bands at 1670 (sh), 1665 (vs, conjugate C=O), 1612 (s, ArC=C), 1600 (s), 855 (vs, mesityl), 730 (s), and 698 (m, monosubstituted phenyl). The ir spectrum of the material showed the same bands as those in a spectrum of an authentic sample of V. A mixture melting point with authentic V was undepressed. ^{1}H nmr[45,58b] spectral assignments (15% w/v in CCl_4) were 8.15 (AB pattern), 7.6 (A_2B pattern, $C_6\mathbf{H}_5$), 6.83 (2, Mes-$\mathbf{H}_2$), 2.30 (3, *p*-C$\mathbf{H}_3$), 2.22 (6, *o*-C$\mathbf{H}_3$). The compound formed a 2,4-dinitrophenylhydrazone derivative, mp 234–236° (lit.[14] 232.0–232.5°), ir 1668 cm^{-1} (Nujol) (C=O).

Benzaldehyde, mesitoic acid, V, and water were also obtained on heating hydroperoxide III at atmospheric pressure in a flask maintained at 150° (oil bath temperature); decomposition occurred in a few minutes under these conditions. Heating was continued for 6 hr at 100–110° (1 mm) to obtain a distillate (consisting of benzaldehyde and water) and a sublimate (consisting of mesitoic acid and V). A sticky brownish residue whose ir spectrum showed a carbonyl band at 1815 cm^{-1} remained in the flask. The residue appeared to be a complex mixture as evidenced by tlc and was not investigated further.

A solution of peroxide III in CH_2Cl_2 (or $CHCl_3$) was injected into a silicone oil–firebrick vpc column at 200° (240° injector temperature) using helium as carrier gas. Retention time of the benzaldehyde peak was 1.75 min; the peak position was verified by observing the increase in size when a mixture of benzaldehyde and III were injected. No decomposition was observed when the column temperature was at 131° (150° injector temperature).

Quantitative Analysis of Products.—The procedure for a typical run is given. Final procedures were developed after first conducting numerous preliminary experiments in order to optimize yields. Hydroperoxide III (0.175 g, 6.47×10^{-4} mol) covered with glass wool (in order to minimize scattering of III by decomposition) was decomposed in an erlenmeyer flask maintained at 150° (oil bath temperature). The sample turned yellow on decomposition. The flask was removed from the oil bath and the contents were dissolved in sufficient ethanol to make a volume of 25 ml. The amount of mesitoic acid in this mixture was determined by titrating 3-ml portions (diluted with 3 ml each of water and ethanol) with standard aqueous sodium hydroxide using a pH meter.[62] The amount of mesitoic acid in this solution found was 56 mg (53% yield). For two additional experiments with 200 and 222 mg of III, 57 and 62 mg yields were obtained respectively, corresponding to yields of 47 and 46% mesitoic acid. In a separate experiment, it was found that mesitoic acid and benzaldehyde were formed in nearly equivalent

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(46) Preparation by J. G. L.

(47) It should be emphasized that these are not melting points but decomposition points as evidenced from DSC and DTA studies.

(48) Preparation by M. Z. H.

(49) Analysis by Galbraith Laboratories, Knoxville, Tenn.

(50) Analysis by M-H-W Laboratories, Garden City, Mich.

(51) Band did not disappear when solution was diluted.

(52) E. P. Kohler, *Amer. Chem. J.*, **38**, 511 (1907), reported mp 63°.

(53) A. N. Nesmeyanov, V. A. Sazonova, and E. B. Landor, *Dokl. Akad. Nauk SSSR*, **63**, 395 (1948) [*Chem. Abstr.*, **45**, 2902 (1951)], reported mp 82°.

(54) Since Kohler and Thompson[9] reported mp 116–117° for their product, the product in the present work (from two separate preparations) was repeatedly recrystallized from the following solvents: *n*-hexane, an ether–petroleum ether mixture, ethanol, methanol, benzene, and a carbon tetrachloride–petroleum ether mixture without a change in the 100–101° mp. The same preparation was also previously carried out[55] in our research group to obtain a product with mp 103.2–103.8° dec (from petroleum ether).

(55) K. K. Lum unpublished work.

(56) Broad peak sharpens to singlet on addition of water.

(57) Assigned tentatively on basis of Dailey and Shoolery's rules.[58a]

(58) R. M. Silverstein and G. C. Bassler "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1963: (a) p 87, (b) pp 59–62.

(59) Melting point of mesitoic acid (Aldrich Chemical Co.) 155°; P. Jannech and M. Weiler, *Chem. Ber.*, **27**, 3446 (1894), reported mp 153–153.4°.

(60) Eastman chromatographic sheet with fluorescent indicator coated with silica gel in benzene: methanol (4:1 ratio).

(61) R. C. Fuson and R. W. Hill, *J. Org. Chem.*, **19**, 1575 (1954).

(62) Control experiments with authentic mesitoic acid were performed to check the accuracy of this procedure.

amounts[63] from decomposition of III; the amount of mesitoic acid in the mixture of decomposition products was determined by titration and the amount of benzaldehyde in the mixture was obtained from a uv absorbance–concentration plot prepared from authentic benzaldehyde λ_{max} 330 mμ in *n*-hexane.

The amount of mesityl phenyl diketone (V) in the above ethanol solution (25 ml) was determined by spectroscopic analysis using the peak at λ_{max} 400 mμ and an absorbance–concentration plot prepared from authentic V. The amount of V determined in this way was 18 mg (11% yield). For two further decompositions using 200 and 222 mg of III, 22 and 23 mg yields of V were obtained corresponding to 12 and 11% yields, respectively.

Oxidation of Benzyl Mesityl Ketone (II) to Mesityl Phenyl Diketone (V) during Attempted Methylation of Derived Bromo Grignard Reagent of II.—The derived bromo Grignard reagent of II (3.24 g, 7.80×10^{-3} mol) in anhydrous diethyl ether (50 ml) was placed in a round bottom flask equipped with stirrer, dropping funnel, and drying tube. Methyl iodide (2.28 g, 1.61×10^{-2} mol) was added with stirring. Anhydrous tetrahydrofuran (50 ml) was added to increase solubility of the derived Grignard reagent; diethyl ether was removed by distillation. More methyl iodide (2.28 g, 1.61×10^{-2} mol) was added. After standing overnight, ether (20 ml) and water (2 drops) were added. The reaction mixture was dried with anhydrous sodium sulfate and solvents were removed with a rotary evaporator. A reddish-brown oil remained from which yellow crystals of V deposited after standing for 2.5 days. V was recrystallized from methanol in 0.138 g yield (7.9%), mp 135–138°.[64] The ir spectrum[44] of V (Nujol mull) showed bands at 1661 (vs) and 1675 (sh, $C=O$), 1610 (s), 1595 (s), 851 (vs), 721 (s), and 699 cm^{-1} (m). V formed a mono-2,4-dinitrophenylhydrazone derivative which was recrystallized from 95% ethanol, mp 234–236° (lit.[14] 232–232.5°). The ir spectrum[44] of the mono-2,4-dinitrophenylhydrazone (Nujol) showed bands at 3275 (w), 1675 (s, $C=O$), 1612 (s), 1601 (s), 1510 (s), 1360 (s), 1308 (s), 920 (w), 912 (w), 848 (m), 843 (w), 740 (s), and 695 cm^{-1} (m).

Instruments and Measurements.—^{1}H nmr spectra were obtained with a Varian Associates DP-60 spectrometer. Tetramethylsilane was used as an internal standard. Chemical shifts were determined from side bands generated by a Hewlett–Packard wide range oscillator (Model 200 CDR) and calibrated against the chemical shift of neat acetaldehyde reported[65] as 455.7 ± 1.0 cps. Ir spectra were taken on Baird-Atomic (Model KM-1) and Perkin-Elmer (Model 337) spectrophotometers. Spectra were calibrated with bands from polystyrene film. Uv spectra were recorded with a Beckman DK-1 instrument. Vpc curves were obtained with a Wilkens Aerograph Model A-90 instrument using a silicone oil (GE-76) coated firebrick column.

The instrument for differential thermal analysis was similar to one designed by Stone.[66] The sample holder was constructed of high heat conductivity Inconel containing two holes, one for the sample and one for alumina which was used as inert reference material. Temperature differences between sample and reference were detected with a differential thermocouple of Pt–Pt + 10% Rh and recorded as a function of time. Samples were run as mixtures with alumina and also without added alumina. A Perkin-Elmer DSC-1B instrument was used for differential scanning calorimetry measurements. Temperatures were calibrated with an indium standard. Samples were sealed in aluminum capsules. An empty aluminum capsule was sealed and used as a reference.

Registry No.—3,3-Diphenyl-2-hydroperoxy-2′,4′,6′-trimethylpropiophenone, 25056-05-7; II, 1889-72-1; III, 25056-04-6; IV, 25056-06-8; V, 25056-07-9.

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[63] In an experiment performed in one of the earlier decompositions before the procedure was optimized, 33% mesitoic acid and 32% benzaldehyde were obtained. This decomposition was carried out using an oil bath at 200°, distilling the products *in vacuo* (*ca.* 1 mm). Volatile products were trapped at liquid air temperature, dissolved in *n*-hexane, and analyzed from absorption at 330 mμ for benzaldehyde. The residue was dissolved in ethanol, an equal volume of water was added, and the solution was titrated with standard sodium hydroxide for mesitoic acid.

[64] Mp 136–137° is reported[14] for material obtained from selenium dioxide oxidation of II.

[65] S. L. Manatt and D. D. Elleman, *J. Amer. Chem. Soc.*, **83**, 4095 (1961).

[66] R. D. Stone, The Ohio State University Studies, Eng. 20, No. 4, Eng. Expt. Sta. Bull. No. 146, 77, 1951. A full description is in C. C. Chou, Ph.D. Dissertation, Baylor University, 1968. The authors express appreciation to Professor J. L. McAtee, Jr., and Mr. C. C. Chou for use of the DTA equipment.