Model A-60D spectrometer with tetramethylsilane as an internal reference. Glpc analyses were carried out on a Microtek Model GC-2000R linear temperature programmed gas chromatograph using 0.25 in. × 10 ft coiled stainless steel tubes packed with 20% Carbowax 20M on 60–80 mesh nonacid-washed Chromosorb W. The carrier gas in these determinations was helium, and the temperature program was 50–225° at a rate of 10 deg/min.

General Procedure.—After a three-necked Pyrex flask equipped with Dry Ice condenser and mercury trap, mechanical stirrer, and gas-inlet tube was flushed with dry nitrogen, 2-methylfuran (2) or furfuryl alcohol (3) was added. The desired amount of methylamine was then condensed in the flask, and the calculated amount of $^1/_8$-in. lithium wire was added to the stirred mixture. The solution was decomposed with ammonium chloride in water, and the product was extracted with ether and dried (Na₂SO₄). The solvent was distilled off under vacuum without heat, the products were analyzed by glpc, and the compounds were identified by comparison of their ir and, where noted, nmr spectra with those of authentic compounds.[20] The results of the reduction of 2-methylfuran and furfuryl alcohol are summarized in Tables I and II, respectively.

Reduction of 2-Methylfuran (2).—Following the general procedure above, 20.5 g (0.250 mol) of 2 and 10.35 g (1.50 g-atoms of lithium in 500 ml of methylamine were allowed to react for 8 hr. After extraction (methyl n-propyl ether), 23.3 g of reduced material was recovered. The major products, in order of their elution from glpc, were tetrahydro-2-methylfuran[21] (7.1%) ethanol[21] (7.7%), 2-pentanone[21] (31.6%), N-1-methylbutylidenemethylamine[21] (29.1%), 2-pentanol[21] (17.7%), and 1-pentanol[21] (6.8%). Their relative retention times were 1:2.26:2.64: 2.93:3.89:5.14.

N-1-Methylbutylidenemethylamine (4).—Using a modification of Tiollais' method[9] for preparation of N-alkylaldimines, 40.5 g (0.472 mol) of 2-pentanone was added dropwise to 150 ml of methylamine and stirred for 1.5 hr. The excess methylamine was removed by heating to 50°. Addition of potassium carbonate caused foaming and separation into two layers. The organic layer was decanted, diluted with an equal volume of ether, and dried (Na₂SO₄). A 45–50% yield of 4, bp 108–110°, was realized:[22] ir $\nu_{max}^{CCl_4}$ 2962, 2879, 1451, 1358 (CH), and 1659 cm⁻¹ (C=N); nmr (CCl₄, max) τ 6.90 (s, 3, C=NCH₃), 7.39–8.80 (complex m, 7, CH₂ and CH₃), and 9.06 (t, 3, CH₃).

Reduction of N-1-Methylbutylidenemethylamine (4). A. Catalytic Hydrogenation of Authentic 4.—An 8.80-g mixture of 4 and 2-pentanone was allowed to react in a Parr hydrogenation apparatus[23] until detectable reaction ceased (5.5-psi decrease). The final product mixture, analyzed by glpc, was composed of 2-pentanone (18.2%), 2-pentanol (23.2%), and N,1-dimethylbutylamine (58.6%).

The spectral data for N,1-dimethylbutylamine follow: ir $\nu_{max}^{CCl_4}$ 2966, 2935, 2875, 2791, 1467, 1372 (CH), 3263 (NH, very weak), and 1161 cm⁻¹ (CN); nmr (CDCl₃, max) τ 7.58 (s, 3, NCH₃) and 8.33–9.30 (complex m, 11, CH, CH₂, and CH₃).

Anal. Calcd for C₆H₁₅N: C, 71.21; H, 14.94. Found: C, 70.95; H, 14.77.

B. Catalytic Hydrogenation of 4 from the Reduction of 2-Methylfuran (2).—In a Brown[2] Micro Hydro-Analyzer[24] was placed 4.0 mg (0.0403 mmol) of 4. The reduction, which consumed 0.0400 mmol of the theoretical 0.0403 mmol of hydrogen, produced N,1-dimethylbutylamine identical with that obtained from reduction of the authentic 4.

C. Reduction of 4 with Lithium in Methylamine.—Using the general procedure (*vide supra*), an 18.5-g mixture of 0.1 mol of 2-pentanone, 0.1 mol of 4, 2.76 g (0.400 g-atom) of lithium, and 400 ml of methylamine were stirred together for 5 hr and 10 min. The 17.0-g product mixture, analyzed by glpc, was composed of N,1-dimethylbutylamine (54.7%), 2-pentanol (7.9%), 2-pentanone (13.3%), and 4 (24.2%).

Reduction of Furan (1).—After 8 hr, the reaction of 34.0 g (0.500 mol) of freshly distilled furan and 20.7 g (3.00 g-atoms) of lithium in 1000 ml of methylamine yielded 21.9 g of reduced material. This was composed of N-butylidenemethylamine[21] (64.9%), 1-butanol[21] (25.0%), N-(2-ethyl-2-hexenylidene)-

methylamine[21] (6.1%), and N-(2-ethyl-3-methylaminohexylidene)methylamine (4.0%).

N-Butylidenemethylamine (6)[9] gave the following spectral data: ir $\nu_{max}^{CCl_4}$ 2969, 2878, 2846, 1457 (CH), and 1672 cm⁻¹ (C=N); nmr (CDCl₃, max) τ 2.35 (perturbed s, 1, CH=N), 6.73 (perturbed s, 3, C=NCH₃), and 7.66–9.31 (complex m, 7, CH₂ and CH₃).

N-(2-Ethyl-2-hexenylidene)methylamine (8)[11] gave the following spectral data: ir $\nu_{max}^{CCl_4}$ 2972, 2945, 2882, 2849, 2777, 1463, 1456, 1402 (CH), 1644 (C=N), and 1633 cm⁻¹ (C=C); nmr (CDCl₃, max) τ 2.28 (perturbed s, 1, CH=N), 4.25 (t, 1, CH=C), 6.64 (s, 3, C=NCH₃), 7.69 (perturbed quintet, 4, C=CCH₂), and 8.28–9.28 (complex m, 8, CH₂ and CH₃).

N-(2-Ethyl-3-methylaminohexylidene)methylamine (7) gave the following spectral data: nmr (CD₃COCD₃, max) τ 4.38 (perturbed s, 1, CH=N), 6.47–6.77 (complex m, 1, CHC=N), 7.52 (s, 3, C=NCH₃), 7.85 (s, 3, NDCH₃), and 8.00–9.32 (complex m, CH, CH₂, and CH₃).

N-Pentylidenemethylamine was prepared using the procedure for the preparation of N-1-methylbutylidenemethylamine, and gave the following spectral data: ir $\nu_{max}^{CCl_4}$ 2958, 2880, 2863, 2846, 2781, 1459 (CH), and 1671 cm⁻¹ (C=N); nmr (CCl₄, max) τ 2.43 (br s, 1, CH=N), 6.83 (perturbed s, 3, C=NCH₃), and 7.37–9.31 (complex m, 9, CH₂ and CH₃).

Registry No.—**1,** 110-00-9; **2,** 534-22-5; **3,** 98-00-0; **4,** 22431-09-0; **7,** 22431-11-4; N-1-dimethylbutylamine, 22431-10-3; N-pentylidenemethylamine, 10599-75-4.


Diphenylmethyl Bishydroperoxide.
An Anomalous Product from the Ozonolysis
of Tetraphenylethylene

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The ozonolysis of an olefin in a hydroxylic solvent is one method of synthesizing alkoxy hydroperoxides.[2–4] Tetraphenylethylene has been ozonized in the presence of methanol,[5,6] but the resultant methoxy hydroperoxide from the interception of the Criegee zwitterion (2) has never actually been isolated. We have made numerous attempts to prepare the expected methoxy hydroperoxide at temperatures ranging from −78 to 0° and have isolated only the expected benzophenone and the completely unexpected diphenylmethyl bishydroperoxide (1). A bishydroperoxide during ozonation in a hydroxylic solvent has not been previously observed.

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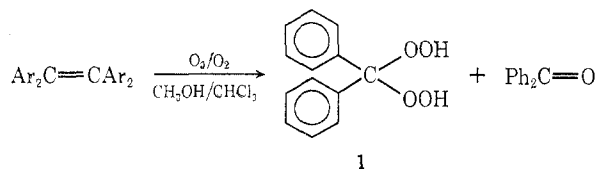
(1) National Science Foundation Graduate Teaching Assistant Fellow, summers of 1968, 1969.

(2) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(3) R. Criegee and G. Lohaus, *Ann. Chem.*, **583**, 6 (1953).

(4) R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 34.

(5) S. Fliszar, D. Gravel, and E. Cavalieri, *Can. J. Chem.*, **44**, 67 (1966).

(6) S. Fliszar and M. Granger, *J. Amer. Chem. Soc.*, **91**, 3330 (1969).

(20) Unless otherwise noted, the authentic samples were obtained from commercial sources.

(21) Nmr spectra were used for identification.

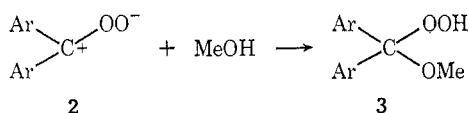(22) This yield is based on glpc analysis of the product mixture.

(23) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1957, p 867.

(24) C. A. Brown, *Anal. Chem.*, **39**, 1882 (1967).

The aliphatic bishydroperoxides are usually prepared by the action of hydrogen peroxide on the ketone (acetone,[7] ethyl methyl ketone,[8] diethyl ketone,[9] and cyclohexanone[10-12]). Cadogan, *et al.*,[13] may have observed 1 from the reaction of 85% hydrogen peroxide. with benzophenone. They isolated a peroxide, mp 90–92°, but did not establish the structure of the compound. Our attempts to reproduce this synthesis under a variety of conditions were unsuccessful.

Results and Discussion

Ozonolysis of tetraphenylethylene in a chloroform–alcohol solution produced, after removal of the solvent, a clear, colorless oil. Tlc analysis of this oil, on silica gel at −5° indicated the presence of only two components in the mixture. One would expect these to be, based on previously reported work,[2-6] benzophenone and diphenylmethoxy methyl hydroperoxide 3 (or the ethoxy derivative, depending on the alcohol used in the solvent system). We were able to isolate both compo-

$$\begin{array}{c}Ar\\Ar\end{array}\!\!\!C\!\!\!\begin{array}{c}OO^-\\+\end{array} \;+\; MeOH \;\longrightarrow\; \begin{array}{c}Ar\\Ar\end{array}\!\!\!C\!\!\!\begin{array}{c}OOH\\OMe\end{array}$$
$$\qquad\;\; 2 \qquad\qquad\qquad\qquad\qquad 3$$

nents of the mixture and readily identified one as benzophenone. The other component, a white crystalline solid, gave ir and nmr spectra which were not compatible with 3. The ir spectrum showed no aliphatic C–H absorptions in the 2900-cm^{-1} region while the nmr gave no indication of any aliphatic protons. A multiplet was observed at δ 7.25–7.73 and a broad singlet at 9.70 (integration ratio 5:1) which disappeared on addition of D$_2$O. The white solid reacted readily with starch–iodide paper, and a quantitative titration for active oxygen gave an equivalent weight of 60.8 (equivalent weight of 3 is 115). Owing to the overwhelming evidence against 3 it was rejected as the structure for the other component in the ozonolysis mixture.
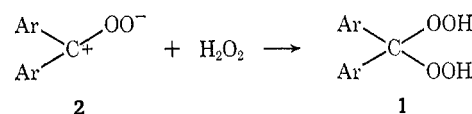
Structure 1 fits the experimental evidence much better than does 3. The equivalent weight of 1 is 58, and for the nmr spectrum one would expect a multiplet due to the aromatic protons and a broad singlet downfield, integrating in the ratio of 5:1, as was observed. In addition, the ir spectrum is compatible with what would be expected for structure 1. Confirmation for structure 1 was obtained from a low temperature mass spectrum which gave a parent ion of mass 232, the molecular weight of 1, intensity 1%.

Chemical evidence for 1 was obtained from the thermal behavior and pyrolysis products of the white solid. Compound 1 readily converts to benzophenone and oxygen on heating. For example, a KBr pellet of 1 was prepared and the ir spectrum obtained, but after heating the pellet for 20 min at 130° a new spectrum was obtained. These two ir spectra were com-

pletely different, and the latter was superimposable on the ir spectrum of benzophenone, with the exception of a few very weak peaks due to residual 1. In addition, when 1 was decomposed in the gas chromatograph only two peaks resulted, which by comparison with authentic samples were identified as benzophenone and oxygen. Again, these results were confirmed by mass spectrometry. A moderate temperature (source 130°) mass spectrum of 1 gave only the spectrum of benzophenone and a large oxygen 32 peak.
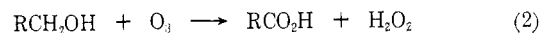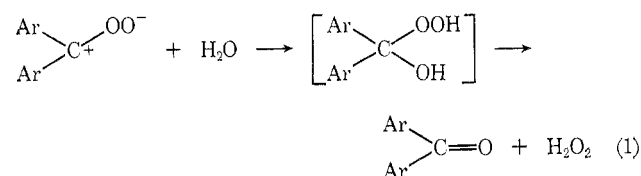
This thermal instability of 1, while expected, made meaningful elemental analysis difficult and accounts for the somewhat high equivalent weight obtained. However, an acceptable analysis was obtained for the diacetyl derivative.

The bishydroperoxide was thought to be formed by the reaction of 2 with hydrogen peroxide. To test this

$$\begin{array}{c}Ar\\Ar\end{array}\!\!\!C\!\!\!\begin{array}{c}OO^-\\+\end{array} \;+\; H_2O_2 \;\longrightarrow\; \begin{array}{c}Ar\\Ar\end{array}\!\!\!C\!\!\!\begin{array}{c}OOH\\OOH\end{array}$$
$$\qquad\;\; 2 \qquad\qquad\qquad\qquad\qquad 1$$

hypothesis 2 drops of 90% H$_2$O$_2$ was added to the reaction mixture before ozonolysis and the yield of isolatable bishydroperoxide increased from 50 to 71%. However, when the hydrogen peroxide was added to the ozonolysis product mixture after removing the solvents, no increase in the yield of 1 was observed. Apparently 1 is formed during the ozonolysis reaction and not from decomposition of some intermediate such as 3.

There are at least two possible sources of H$_2$O$_2$ in this system, as shown by reactions 1 and 2. Reaction 1

$$\begin{array}{c}Ar\\Ar\end{array}\!\!\!C\!\!\!\begin{array}{c}OO^-\\+\end{array} + H_2O \longrightarrow \left[\begin{array}{c}Ar\\Ar\end{array}\!\!\!C\!\!\!\begin{array}{c}OOH\\OH\end{array}\right] \longrightarrow$$
$$\begin{array}{c}Ar\\Ar\end{array}\!\!\!C\!\!=\!\!O \;+\; H_2O_2 \quad (1)$$

$$RCH_2OH + O_3 \longrightarrow RCO_2H + H_2O_2 \quad (2)$$

requires residual water within the system and may be the source of only a small amount of hydrogen peroxide, while reaction 2 is very likely the main source of hydrogen peroxide. Whiting and coworkers[14] indicate that this reaction occurs readily at −78°.

The results of this investigation indicate that the diphenyl-substituted Criegee zwitterion is quite stable and selective as to its requirements for reaction with a nucleophile. This stability may be due either to a large delocalization energy *via* resonance with the π system of the phenyl rings or to the formation of the dioxirane intermediate 4. At any rate, neither the

$$\begin{array}{c}Ar\\Ar\end{array}\!\!\!C\!\!\!\begin{array}{c}O\\O\end{array}$$
$$4$$
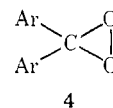
(7) N. A. Milas and A. Golubovic, *J. Amer. Chem. Soc.*, **81**, 6461 (1959).
(8) N. A. Milas and A. Golubovic, *ibid.*, **81**, 5824 (1959).
(9) N. A. Milas and A. Golubovic, *ibid.*, **81**, 3361 (1959).
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(13) J. I. G. Cadogan, D. H. Hey, and W. A. Sanderson, *J. Chem. Soc.*, 4897 (1960).

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ozonide, the alkoxy hydroperoxide, nor the Criegee zwitterion dimer forms when better nucleophiles are present.

Experimental Section

Ozonolysis Procedure.—An Orec O_3V_2 ozone generator was used. The concentration of ozone was about 1% in oxygen with a flow rate of 1.5 l./hr. The O_2 was dried prior to entering the generator by passing it through concentrated sulfuric acid. The O_3–O_2 mixture was passed into the reaction system which had been previously cooled to $-78°$ with a Dry Ice–acetone slurry.

Tetraphenylethylene (1.00 g, 3.01 mmol), mp 221–224°, was dissolved in 150 ml of chloroform (distilled) and 100 ml of methanol (distilled over magnesium) or ethanol, and treated with ozone until the appearance of blue color in the solution indicated excess ozone (*ca.* 20 min). The excess ozone was then flushed out with nitrogen. The solvent was stripped off (10–20 mm and 10–20°) leaving a clear, colorless oil. Tlc of the oil at $-5°$ on silica gel and developed with $CHCl_3$ indicated two compounds identified as benzophenone and 1: yield 0.71 g, 3.90 mmol, of benzophenone and 0.35 g, 1.51 mmol (50%), of bishydroperoxide.

Diphenylmethyl Bishydroperoxide (1).—After recrystallization from hexane, the white needles of 1 had a melting point of 94–96°. A reaction with starch–iodide paper indicated that the compound contained active oxygen. The infrared spectrum showed no absorption in the carbonyl region but strong bands were observed at 3450, 1450, 1205, 1040, 781, 741, and 704 cm⁻¹. The nmr spectrum in acetonitrile showed two types of protons, a broad singlet at 9.70 and a multiplet at δ 7.25–7.73, which integrated 1:5, respectively. The addition of 2 drops of deuterium oxide to the nmr tube caused the singlet at δ 9.70 to disappear. A low-temperature (source at 50 $\pm$ 2°) mass spectrum established the parent ion at 232 (1% intensity) with major peaks at 77, 105, 182, and 199. Elemental analysis was not satisfactory owing to facile decomposition to benzophenone. The diacetyl derivative was formed by adding acetyl chloride to a pyridine solution of 1. The resulting diperester was recrystallized from hexane giving white needles (mp 109.5–111.0°). The nmr spectrum of the perester showed a singlet at δ 1.88 and a multiplet at 7.20–7.65 integrating 6:10, respectively. The infrared spectrum had a strong carbonyl band at 1785 cm⁻¹, characteristic of peresters.[15,16] A high resolution mass spectrum of the perester with the internal standard, heptacosafluorotributylamine, established the parent ion at 316 (0.3% intensity). *Anal.* Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10; O, 30.35. Found: C, 64.68; H, 5.23; O, 30.24.

Analysis for Active Oxygen.—An analytical technique developed at this laboratory was used to determine active oxygen content. Titrations were carried out in a 125-ml erlenmeyer flask equipped with a gas inlet stem at the bottom. During a titration nitrogen was passed into the titration vessel through a gas washing bottle filled with crushed Dry Ice. A sample (13 mg) was added to 25 ml of glacial acetic acid containing 1 g of KI. After 15 min in the dark (under carbon dioxide–nitrogen), 80 ml of water was added and the iodine titrated with 0.01 N sodium thiosulfate. A blank titration was unnecessary. The titrated solution remained colorless until the gas system was turned off (1 hr later). This technique was very reproducible (equiv wt: 60.41, 61.27) and, based on our results, appears superior to that used by Fliszar and Granger,[6] eliminating iodine entrapment by solid ice, air oxidation of the iodide ion, and titration at near 0°.

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1964, p 129.
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9H-Dibenz[c,f]imidazo[1,2-a]azepines

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In connection with another investigation, we attempted to effect the cyclodehydration of the benzamide (*viz.* 1) into the 7 position of the indoline nucleus. After an initial unsuccessful attempt with phosphorus oxychloride, we investigated the reaction of 1 with polyphosphoric acid. The product obtained from this reaction in 38% yield was not the expected cyclodehydration product but an isomer thereof. Based on mechanistic considerations (*vide infra*) and the similarity of its ultraviolet spectrum to that of 2[1] [λ_{max} 256 mμ (ϵ 8120), 295 (6830), and 229 (inflection, 13,930)],
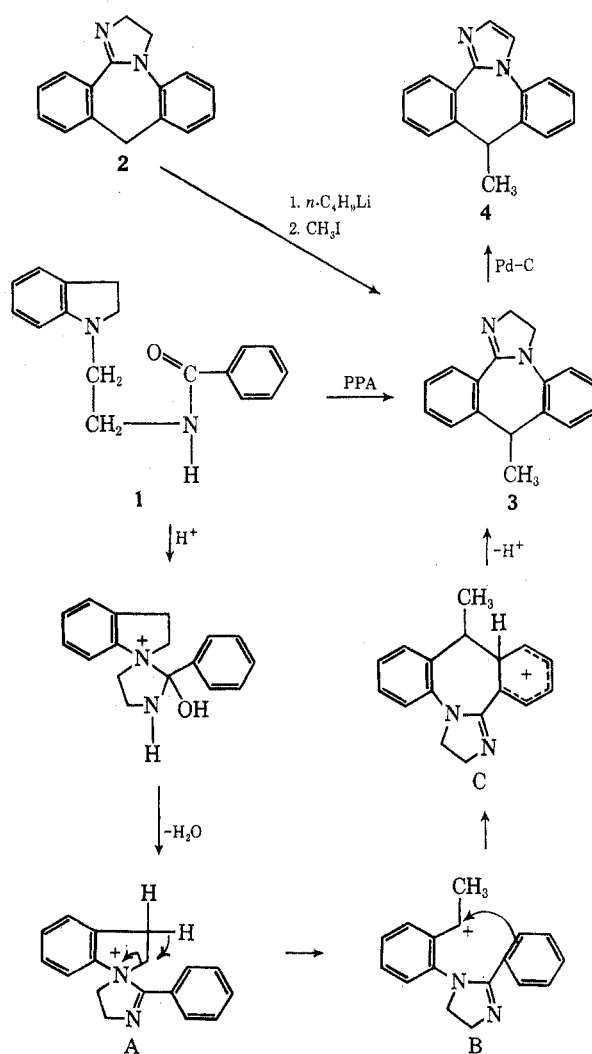
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