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°.

Registry No.—**1**, 22461-45-6; **1**, diacetyl derivative, 22461-46-7; tetraphenylethylene, 632-51-9.

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[15] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1964, p 129.

[16] M. M. Martin and E. B. Sanders, *J. Amer. Chem. Soc.*, **89**, 3777 (1967).

9H-Dibenz[*c*,*f*]imidazo[1,2-*a*]azepines

J. B. Hester, Jr.

Research Laboratories, The Upjohn Company,
Kalamazoo, Michigan 49001

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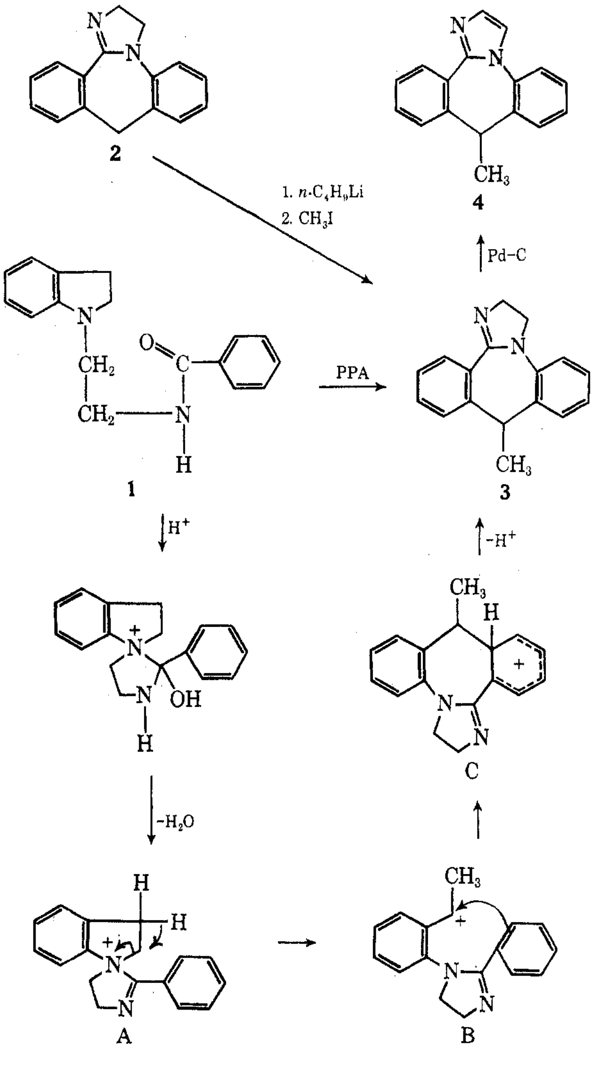
In connection with another investigation, we attempted to effect the cyclodehydration of the benzamide (*viz.* **1**) into the 7 position of the indoline nucleus. After an initial unsuccessful attempt with phosphorus oxychloride, we investigated the reaction of **1** with polyphosphoric acid. The product 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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[1] A. E. Drukker, C. I. Judd, and D. D. Dusterhoft, *J. Heterocycl. Chem.*, **3**, 206 (1966).

we proposed structure **3** for this product. Confirmation of this structure was achieved by an independent synthesis: alkylation of **2**, which was prepared by the literature method, by successive treatment with *n*-butyllithium and methyl iodide gave a product which was identical with **3**.

A mechanistic interpretation of the reaction is shown. Initial cyclodehydration of **1** to form A might be followed by successive cleavage of the CH_2-N^+ bond and hydride migration to give the relatively stable benzylic carbonium ion (B). An electrophilic reaction of this carbonium ion with the monosubstituted benzene ring would lead, *via* C, to the observed product (**3**). A somewhat analogous reaction of N,N-dialkyl-N′-acyl-*o*-phenylenediamines with polyphosphoric acid to give benzimidazoles has been reported.[2]

Initial attempts to degrade **3** by acid (6 *N* HCl) or alkaline (20% ethanolic KOH) hydrolysis were unsuccessful; starting material was recovered in both cases. Palladium-catalyzed dehydrogenation of **3** in refluxing decalin gave **4** in 78% yield.

The nmr spectra of **3** and **4** were interesting in that the methyl group in each case was represented by a pair of doublets. This phenomenon was temperature dependent: at 120° the methyl group of **3** appeared as a doublet and at 140° the methyl group of **4** appeared as a broad singlet with a half band width of *ca.* 22 Hz. This type of behavior is characteristic of molecules which at a given temperature can assume two or more conformations which are relatively stable and slowly interconvertible.[3]

The relative intensities of the doublets for both **3** and **4** were nearly equal, which suggests that in each case the two conformations represented were approximately equally populated at ambient temperature. Molecular models of **3** and **4** show that in the two possible conformations the methyl group would be influenced differently by the electronic environment associated with the neighboring benzene rings; this is consistent with the observed results.

Experimental Section[4]

1-(2-Benzamidoethyl)indoline (1).—A solution of benzoyl chloride (63.5 g, 0.452 mol) in benzene (200 ml) was added during 20 min to a cold, stirred solution of *1-(2-aminoethyl)indoline*[5] (65.8 g, 0.411 mol) and triethylamine (49.7 g) in benzene (820 ml). The resulting mixture was allowed to stand under N_2 at ambient temperature for 18 hr and poured into water (1.5 l.). This mixture was made alkaline with 50% NaOH and extracted with benzene. The benzene extract was dried (K_2CO_3) and concentrated. Crystallization of the residue from EtOAc gave 92.5 g (84.7%) of **1**, mp 99.5–103°. Data for the analytical sample follow: mp 104–104.5°; uv (EtOH) λ_{max} 250 mμ (end absorption, ϵ 13,100), 299 (2750), and 226 (inflection, 13,450); ir (Nujol) 3320 (NH) and 1630 cm^{-1} (C=O).

Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.80; H, 7.02; N, 10.60.

2,3-Dihydro-9-methyl-9H-dibenz[*c,f*]imidazo[1,2-*a*]azepine (3). **A.**—A stirred mixture of **1** (45.0 g, 0.169 mol) and polyphosphoric acid (1.3 kg) was kept under N_2 at 150–160° for 21.5 hr and then poured into stirred ice-water (2–3 l.). The solution which resulted was made alkaline with 50% NaOH and extracted with ether. The ether extract was washed successively with water and brine, dried (K_2CO_3), and concentrated. The residue was chromatographed on silica gel (2 kg) with Et_3N-EtOAc (2:98). The first material eluted was unreacted starting material, 5.12 g, mp 103.5–105°. The product was then eluted and crystallized from EtOAc–Skellysolve B to give 14.6 g, mp 142–143°, and 1.15 g, mp 120–123° (37.6%), of **3**. That the two crops were different polymorphic crystalline forms of the same compound was demonstrated by mixture melting point and ir ($CHCl_3$) comparison. Data for the analytical sample follow: mp 128.5–129°; uv (EtOH) λ_{max} 295 mμ (end absorption, ϵ 8800), 291 (7250), and 233 (inflection, 14,600); mass spectrum *m/e* (rel intensity) 248 (100), 247 (44), 233 (96), and 204 (18); nmr ($CDCl_3$) δ 1.55, 1.73 (two d, 3, J = 7.5 Hz, CH_3CH), 4.05 (m, 5, C-2, -3, -9), 7.16 and 7.86 (two m, 7 and 1, C-5–8 and -10–13); nmr [$(CD_3)_2NCDO$, 120°] δ 1.59 (d, 3, J = 7.5 Hz, CH_3CH) and 3.96 (m, 5, C-2, -3, -9).

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.20; H, 6.50; N, 11.51.

B.—A stirred solution of **2** (2.34 g, 0.0100 mol) in dry tetrahydrofuran (50 ml), under N_2, was treated with 10 ml (0.016 mol) of a 15.13% solution of *n*-butyllithium in hexane. The resulting dark green solution was allowed to stand at ambient temperature for 3.83 hr, cooled in an ice bath, and treated during 8 min with a solution of methyl iodide (0.935 ml, 0.015 mol) in anhydrous ether. This mixture was kept at ambient temperature for 18 hr and poured into ice-water. The resulting mixture was extracted with ether. The ether extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (150 g) with Et_3N-EtOAc (2:98). The product was crystallized from EtOAc–Skellysolve B to give 0.475 g, mp 119.5–122.5°, and 0.506 g, mp 117–119.5° (39.5%), of **3**. The combined product was recrystallized three times from EtOAc, mp 121–124°, identical with the cyclodehydration product (**3**) by ir, uv, and nmr comparison. The mixture melting point was undepressed.

9-Methyl-9H-dibenz[*c,f*]imidazo[1,2-*a*]azepine (4).—A mixture of **3** (1.0 g, 4.03 mmol), 10% palladium on carbon (0.5 g), and decalin (20 ml) was refluxed under N_2 for 15 hr and allowed to stand at ambient temperature for 18 hr. The solid was collected by filtration, washed with Skellysolve B, and extracted with hot MeOH. The MeOH extract was concentrated and the residue was crystallized from EtOAc to give 0.769 g (77.5%) of **4**, mp 167–168.5°. Data for the analytical sample follow: mp 166.5–167.5°; uv (EtOH) λ_{max} 271 mμ (ϵ 11,900); mass spectrum *m/e* (rel intensity) 246 (93), 231 (100), 204 (11), and 177 (9); nmr ($CDCl_3$) δ 1.12, 1.80 (two d, 3, J = 7.5 Hz, CH_3CH), 3.93, 4.09 (two, q, 1, J = 7.5 Hz, CH_3CH), 7.34 and 8.01 (two m, 9 and 1, C-2, -3, -5–8, -10–13); nmr [$(CD_3)_2NCDO$, 140°] δ 1.29 (broad s, 3, CH_3CH), and 4.10 (broad s, 1, CH_3CH).

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.97; H, 5.81; N, 11.68.

Registry No.—**1**, 22922-47-0; **3**, 22922-48-1; **4**, 22922-49-2.

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(2) O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc.*, 2609 (1964).

(3) For example, see J. A. Elvidge in "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press Inc., New York, N. Y., 1967, pp 36–38.

(4) Melting points were taken in capillary tubes and are corrected. The ir spectra were recorded on a Perkin-Elmer Model 421 recording spectrophotometer, the uv spectra on a Cary Model 14 spectrophotometer, and the mass spectra at 70 eV on an Atlas CH-4 spectrometer. The nmr spectra were recorded on a Varian A-60A spectrometer; chemical shifts were measured in parts per million downfield from tetramethylsilane. Skellysolve B is a commercial hexane, bp 60–70°, made by Skelly Oil Co., Kansas City, Mo. The silica gel used for chromatography was obtained from E. Merck AG, Darmstadt, Germany.

(5) R. P. Mull, U. S. Patent 3,093,632 (1963).