$$\log f_{H^+} - \log (f_{XH^+}/f_X) = (1 - \phi_e)[\log f_{H^+} - \log (f_{BH^+}/f_B)] \quad (2)$$

The ϕ_e parameter, depending on free-energy differences, should be a measure of the "external" stabilization of the cation, since the contributions from "internal" stabilization, almost constant through the acid range, should cancel out. Since positive ϕ_e's indicate[3,8,16] a relatively large solvation for the cation, the decrease of its value going from acetone to benzophenone (see Table I) is a measure of the less efficient interaction between the protonated benzophenone and the solvent as a consequence of the increased "internal" charge delocalization into the aromatic rings.

From the above discussion it appears that an inverse relationship should exist between "internal" and "external" stabilization of the oxycarbenium ion. Indeed, a plot of the ^{13}C NMR chemical shift differences reported in Table I vs. the ϕ_e parameters gives a straight line (e.g., for $\Delta\delta^{13}C(FSO_3H)$, slope $= -59.2$, $r = 0.967$).

Although the solvation ability for cations is a well-known property of FSO_3H,[8,15,17] no attempt has been made, at the time of this writing, to separate in this solvent "internal" and "external" contributions to ion stabilization and it is therefore not possible to make a direct comparison between $\Delta H_i(FSO_3H)$ and ^{13}C NMR data. It needs only to be pointed out that the relative energies of solvation for ammonium ions in FSO_3H are[18] within experimental error of those in water. The fact that pK_{BH^+} and $\Delta H_i(FSO_3H)$ values both show the same basicity order for ketones is a further indication of the remarkably similar solvation properties of water and fluorosulfuric acid.[18]

The ^{13}C and protonation data lead to the same conclusion that, as expected, the positive charge is more delocalized in the benzophenone than in the acetone-derived oxycarbenium ion. As a consequence, the "internal" or intrinsic stabilization decreases in the same order. The overall stabilization of an ion, as evaluated in solution from dynamic measurements such as protonation equilibria or kinetics, is, however, a combination of "internal" and "external" (that provided by interactions with the solvent) stabilization.[19] The "external" stabilization varies inversely with the "internal" one, since it is an inverse function of the charge density in the cation, and obviously depends on the nature of the solvent. It is therefore of paramount importance, when considering dynamic measurements, to clearly identify the role played by the solvent and that by the substituents in the stabilization of charged species.

Experimental Section

The five ketones studied were reagent grade commercial products, purified by crystallization or distillation until their physical constants agreed with accepted literature data.[20] The acid solutions were made by diluting with distilled water the commercial reagent grade sulfuric acid and standardized by titration with NaOH. The H_0 values were interpolated from published data.[21] The NMR spectra were recorded at 25 °C (±0.3 °C) on a Bruker HFX-10 or a Bruker WP-60 spectrometers and the UV spectra on a Cary 15 spectrophotometer equipped with a thermostated cell compartment (25 ± 0.2 °C). The solutions for the UV spectra were prepared by dissolving 0.12 g of ketone in CH_2Cl_2 (100 mL). Aliquots (5 mL) were then transferred in a 50-mL volumetric flask, the solvent was removed at reduced pressure, and the residual ketone was dissolved in the thermostated acid of the appropriate concentration. The titration curves were obtained, following the Davis and Geissman method,[22] by plotting the differences in absorbance at 258 and 342 nm [$\Delta A = A_{258} - A_{342}$] as a function of the medium acidity, expressed by H_0. The ionization ratios were computed as $I = (\Delta A_B - \Delta A)/(\Delta A - \Delta A_{BH^+})$, where ΔA_B and ΔA_{BH^+} are the differences in absorbance for the free base and its conjugate acid, as obtained from the linear part of the titration curve at low and high acidity, respectively. The solutions for the NMR measurements were made by dissolving ~20 μL of ketone in 2 mL of the sulfuric acid solutions containing $Me_3NH^+HSO_4^-$ as internal standard. The chemical shifts were measured as the difference between the methyl resonance of the methyl ketones and that of the internal standard ($\Delta\nu = \nu - \nu_{ref}$). Because of its low solubility in aqueous acid solutions, the NMR spectra of dicyclopropyl ketone were recorded on the Bruker WP-60 pulsed spectrometer. In this case we have monitored the peak of highest intensity in the complex multiplet of the cyclopropyl resonance. Plots of $\Delta\nu$ vs. H_0 give good sigmoid curves from which the ionization ratios were obtained as described in our previous papers.[3,16]

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1,4-Dimethyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene: Synthesis and Characterization[1]

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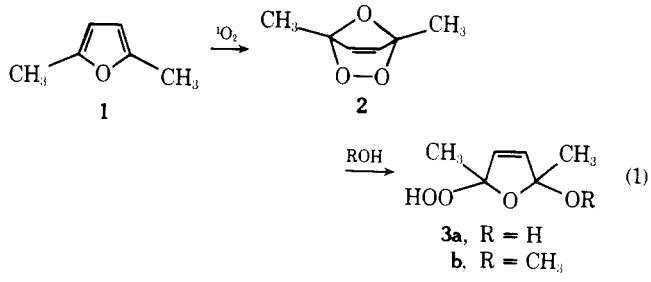
The use of 2,5-dimethylfuran (1) as a diagnostic test for singlet oxygen in chemical and especially biological systems is amply documented.[3] For example, the formation of 2,5-dimethyl-2-hydroperoxy-5-hydroxydihydrofuran (**3a**) from **1** in the acetaldehyde–xanthine oxidase system was construed as evidence that the endoperoxide **2** intervened as the enzymatic singlet oxygenation product of **1** (eq 1).[4] In fact, for-



1 2

(1)

3a, R = H
b, R = CH_3

mation of **3b** in the photosensitized oxygenation of **1** with methanol as solvent[5] lent credence to this supposition. Indeed, gas-phase singlet oxygenation of **1** and condensing the product stream onto a liquid nitrogen cold finger gave the monomeric endoperoxide **2**; but on warming above −30 °C it quickly polymerized with oxygen evolution.[6] We now provide evidence that the monomeric endoperoxide **2** can be formed quantitatively on photosensitized singlet oxygenation of **1** in CCl_4 or $CFCl_3$ at 0–5 °C, and contrary to previous reports[5,6] it is remarkably stable in solution even at room temperature (ca. 25–30 °C). Our evidence includes the following: (1) a 99.3% peroxide titer (iodometry) based on **2**; (2) low temperature bulb-to-bulb codistillation with CCl_4; (3) conversion into the hydroperoxide **3b** on treatment with methanol; and (4) quantitative deoxygenation into 1,2-diacetylethylene with triphenylphosphine. The experimental details are described below.

Experimental Section

Melting points are uncorrected. NMR spectra were run on a Hitachi Perkin-Elmer Model R-24B instrument and IR spectra on a Perkin-Elmer Model 237B Infracord. Solvents and reagents used were purified according to standard literature procedures.

2,5-Dimethylfuran Endoperoxide (2). The irradiation was carried out in a 50-mL, two-neck, round-bottom flask provided with a magnetic spinbar, a rubber septum, and a gas inlet tube which was connected to an oxygen-filled balloon. The flask was charged with a solution of 2,5-dimethylfuran (ca. 250 mg, 2.60 mmol) and tetraphenylporphyrin (0.5 mg) in 20 mL of CCl_4 (or $CFCl_3$), submerged in a water or ice bath, and positioned as close as possible (~10 cm) to a General Electric 150-W sodium street lamp. While the solution was vigorously stirred by magnetic action, the light source was activated and the required singlet oxygen was generated in situ. Within 120 min the photooxygenation was completed, as confirmed by monitoring the progress of the reaction by NMR. The characteristic furan proton resonances (CCl_4, Me_4Si) at δ 5.58 (olefinic, singlet, 2 H) and 2.17 (methyl, singlet, 6 H) were replaced by the characteristic peaks at δ 6.02 (olefinic, singlet, 2 H) and 1.70 (methyl, singlet, 6 H), respectively, of the endoperoxide **2**. The IR spectrum (CCl_4) showed bands at 3080 (olefinic CH), 2990, 2940 (aliphatic CH), 1450, 1390, 1330, and 1210 cm^{-1}. Iodometric analysis of the solution gave a 99.3 ± 0.5% peroxide titer based on the endoperoxide structure **2**. Attempted isolation by solvent removal even at subambient temperatures (~0 °C) afforded polymeric product. However, on flash distillation at −20 °C (0.10 mmHg) the volatile endoperoxide codistilled intact with the CCl_4.

2,5-Dimethyl-2-hydroperoxy-5-methoxy-2,5-dihydrofuran (3b). A solution of the endoperoxide **2** (7.47 mmol) in 20 mL of $CFCl_3$ was cooled to −78 °C by means of a dry ice–acetone bath, and under a N_2 atmosphere 5 mL of anhydrous CH_3OH was syringed in dropwise while the mixture was stirred. After 2 h at −78 °C, the reaction mixture was allowed to warm up to 0 °C and the solvent was removed at 0 °C (10 mm Hg) to afford 410 mg (93.5%) of crude hydroperoxide **3b**. The latter was purified by sublimation at 60–65 °C (0.15 mmHg), mp 74–75 °C (lit.[5] mp 75–76 °C). The ^1H NMR and IR data were identical with those of an authentic sample prepared directly by singlet oxygenation of 2,5-dimethylfuran in methanol.

Triphenylphosphine Deoxygenation of Endoperoxide 2. A solution of the endoperoxide **2** (2.50 mmol) in 20 mL of CCl_4 was cooled to −20 °C, and while under a N_2 atmosphere with stirring a solution of triphenylphosphine (2.50 mmol) in 5 mL of CCl_4 was syringed in at −20 °C for 1 h. The mixture was allowed to warm up to room temperature (ca ~30 °C) and was kept there for 12 h. The product showed the characteristic[4a] 1,2-diacetylethylene proton resonances (CCl_4, Me_4Si) at δ 6.60 (olefinic, singlet, 2 H) and 2.22 (methyl, singlet, 6 H) and IR (CCl_4) bands at 3050 (olefinic C–H), 1680 (C=O), 1430, 1360, 1280, and 1200 cm^{-1}.

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Registry No.—**1**, 625-86-5; **2**, 45722-89-2; **3b**, 13249-74-6; 1,2-diacetylethylene, 4436-75-8.

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New Syntheses of Tetrathiafulvalene

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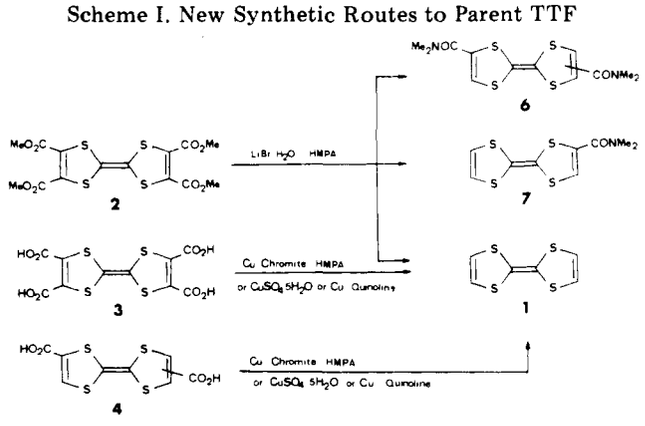
Tetrathiafulvalene (TTF, **1**) is known to be a superior π donor in the formation of highly conducting charge-transfer complexes.[1] Although this compound was first prepared by coupling of the 1,3-dithiolium cation,[2] although the method by Melby, Harzler, and Sheppard[3] seems to be suitable for preparing large amounts of TTF, and although the procedure by Wudl et al.[14] might be preferred for a small scale preparation, we report here new facile syntheses of TTF utilizing tetrakis(carbomethoxy)- (**2**),[5] tetracarboxy- (**3**),[5] and dicarboxytetrathiafulvalenes (**4**),[3,5] which have been prepared during the course of our systematic studies[6] on the reactions of isotrithiones with trialkyl phosphites.

A mixture of tetraester **2** and an excess of lithium bromide monohydrate in HMPA was gradually heated to 80 °C, and the temperature was maintained for 2 h (Scheme I). During this period the mixture was orange-red and gas evolution was observed. Treatment of the mixture with deaerated water gave TTF and bis(carbomethoxy)tetrathiafulvalene (**5**) in 11 and 53% yields, respectively.[7] Compound **5** was identified on the basis of its spectral data.[3,5]

Further reaction at 150–160 °C for 10 min, after the gas evolution ceased, afforded TTF (**1**, 13%), tetrathiafulvalene-bis(*N*,*N*-dimethyl)carbamide (**6**, 22.3%), and tetrathiafulvalene-*N*,*N*-dimethylcarbamide (**7**, 18.5%). The structures of **6** and **7** were determined by their analytical and spectral data. In the ^1H NMR spectrum of **6**, the methyl protons attached to the nitrogen atom and the olefin protons appeared as two singlets at δ 3.10 and 6.63, respectively. Generally, the methyl protons attached to the nitrogen atom of an amide group appear as a doublet because of the prominent contri-

Scheme I. New Synthetic Routes to Parent TTF



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