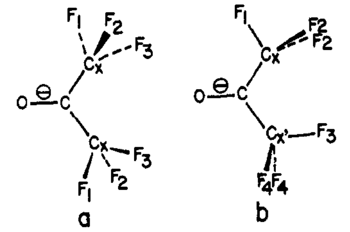
and CF, 1.33 Å. All the atoms except for fluorine are assumed to be planar (*xy* plane) and the bond angles are 120° and 109° 28′. Two presumably stable rotational isomers a and b are considered for each compound.



The fluorine 2s spin densities as well as the π spin density on CO and NO groups and other 2s spin densities are shown in Table I.[6] The ratio of the average fluorine 2s spin density is $\rho_F(\mathbf{1})/\rho_F(\mathbf{2}) = +0.00117/+0.00024 = 4.9$, which is in good agreement with the above-mentioned experimental value of 4.2.[7] This large coupling in **1** can be qualitatively explained in that the half-occupied π MO φ_0 of $[CO]^-$ group has such a high energy (+0.1038 au for $[H_2CO]^-$ in INDO) that it interacts efficiently with the unoccupied π^* MO $\psi_\pi{}^*$ of the CF_3 group which has a low energy (+0.2984 au in HCF_3) because of the large electronegativity of fluorine atoms. In **2**, on the other hand, φ_0 of the NO group is of low energy (−0.4600 au for H_2NO) so that the interaction with $\psi_\pi{}^*$ is small, but is not low enough to interact strongly with occupied π MO's ψ_{π_2} and ψ_{π_3} of the CF_3 group (−0.7126 and −0.7814 au in HCF_3).

Table I. Calculated Spin Densities

Atomic orbital	1a	1b	2a	2b
F_1 2s	+0.00055	−0.00001	+0.00010	−0.00001
F_2 2s	+0.00239	+0.00178	+0.00050	+0.00038
F_3 2s	+0.00057	−0.00003	+0.00011	−0.00003
F_4 2s		+0.00174		+0.00035
F average	+0.00117	+0.00117	+0.00024	+0.00024
C_x and $C_{x'}$ 2s	−0.00181	−0.00183	−0.00105	−0.00105
C or N 2s	+0.00401	+0.00401	+0.00263	−0.00263
O 2s	+0.00454	+0.00454	+0.00439	+0.00439
C or N 2pπ	+0.3008	+0.3008	+0.1694	+0.1694
O 2pπ	+0.6394	+0.6394	+0.8156	+0.1857

Such an abnormality would not be expected in conjugated ketyls[9] in which φ_0 is stabilized by conjugation or in methyl compounds[10] in which the methyl unoccupied π level is of higher energy than the hexafluoromethyl level because of smaller electronegativity of the proton.

The calculated ratio of the trifluoromethyl carbon 2s spin density, $\rho_C(\mathbf{1})/\rho_C(\mathbf{2}) = -0.00182/-0.00105 = 1.7$, compares very well with experimental ratio of the ^{13}C coupling constant,[1b] $a_C(\mathbf{1})/a_C(\mathbf{2}) = 8.0\ G/5.1\ G = 1.6$. In addition, the ratio of the calculated CO carbon 2s to the NO nitrogen 2s spin density, $\rho_C(\mathbf{1})/\rho_N(\mathbf{2}) = +0.00401/+0.00263$, times the ratio of the theoretical splitting[8] for a 2s electron on a ^{13}C atom (1110 G) to that on an ^{14}N atom (550 G) gives the calculated ratio of the coupling constant $a_C(\mathbf{1})/a_N(\mathbf{2}) = 3.1$, which again agrees well with the experimental value,[1b] 23.3 G/8.26 G = 2.8.

Scheidler and Bolton have proposed a hindered rotation of CF_3 groups to explain the temperature dependence of a_F in **2** between 163 and 297°K,[2] and on the other hand a_F in **1** is temperature independent.[1b] The difference of the INDO total energy between **1a** and **1b** gives a rotational barrier of 0.3 kcal/mole, while that between **2a** and **2b** gives 0.6 kcal/mole. This is in qualitative agreement with the hindered rotation mechanism in that the barrier for **2** is larger than for **1**, but cannot explain the temperature dependence of the coupling constant a_F because the average ρ_F in the more stable isomer a is not different from that of b (*cf.* Table I).

Finally it is interesting to note in Table I that for both **1** and **2** the fluorine 2s spin density and therefore the coupling constant a_F can be expressed in good approximation by $a_F = A + B\cos^2\theta$, where θ is the angle between the *z* axis and the projection of the CF bond to a plane perpendicular to the CF_3 axis. This is of the same form as the relationship known for CH_3 proton coupling.[11] *A* is near zero in both compounds, and *B* is a constant which depends on the molecule.

Acknowledgment. The author is grateful to Dr. J. R. Bolton for bringing this problem to his attention and for subsequent stimulating discussions. The calculations were carried out at the Computing Center of the University of Rochester which is in part supported by National Science Foundation Grant GP-7317.

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[6] From the anisotropic ^{14}N hyperfine coupling constant, $\rho^\pi{}_N$ in di-*t*-butyl nitroxide is considered to be approximately 0.5 (J. R. Bolton private communication). The calculated $\rho^\pi{}_N = 0.1694$ for **2** and $\rho^\pi{}_C = 0.3008$ for **1** seem to be too small, but their ratio qualitatively satisfies the experimental implication[1]: $\rho^\pi{}_C > \rho^\pi{}_N$.

[7] In INDO calculation of ethyl radical[4] the average CH_3 proton spin density after annihilation is +0.0347. To obtain the observed coupling constant of +26.87 G, a value of 778 G or 1.53 times 508 G has to be used as the conversion factor. If we use 1.53 times the theoretical value 1.71×10^4 G for fluorine 2s orbitals,[8] the average spin densities 0.00117 and 0.00024 amount to the coupling constants 31.6 and 6.3 G, respectively, which turn out to be reasonably close to the experimental values 34.94 and 8.26 G.

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Triplet Lifetimes of Benzophenone, Acetophenone, and Triphenylene in Hydrocarbons

Sir:

Aromatic ketones, such as benzophenone and acetophenone, are generally considered not to phosphoresce in normal solvents at room temperature,[1] although Parker[2] has recently observed phosphorescence at room temperature from benzophenone in a fluorocarbon solvent. However, the reasonably long lifetime[3] of benzophenone in benzene ($\tau_0 \sim 10^{-5}$ sec) led us to believe that we should be able to see emission in hydrocarbons. This is indeed the case, and in Figure 1 we show the

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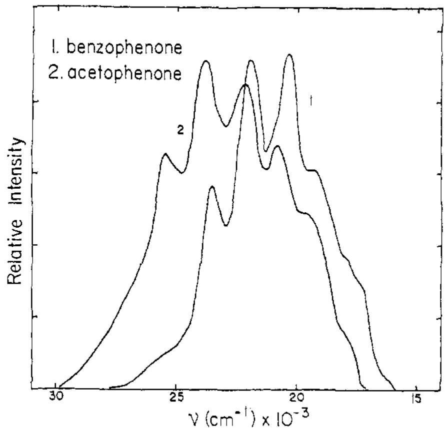

Figure 1. Emission spectra of benzophenone (1) and acetophenone (2) in isooctane at 23°. The intensity is in terms of quanta per unit frequency interval.

emission of benzophenone and acetophenone in isooctane as solvent at 23°. The spectra show good agreement with those obtained in rigid media.[4] The quantum yields of emission were 4×10^{-4} ([benzophenone] $= 1.0 \times 10^{-2}$ M, λ_{excit} 385 mμ) and 4×10^{-4} ([acetophenone] $= 2.0 \times 10^{-3}$ M, λ_{excit} 330 mμ). It will be noticed that the 1000-fold variation in quantum yields of benzophenone and acetophenone in going from the glass at $-196°$ to isooctane at 23° exactly parallels the 1000-fold variation in lifetimes; see Table I ($\Phi_{-196}{}^{\text{benzo}} = 0.74$, τ_0 4.7 msec; $\Phi_{-196}{}^{\text{aceto}} = 0.62$, τ_0 2.3 msec).[5]

Table I. Lifetimes and Naphthalene Quenching Constants for Ketone Triplets at 23°

Solvent	Ketone	$\tau \times 10^6$, sec	$k_q \times 10^9$, M^{-1} sec^{-1}	Method
Benzene	PhCOPh	6.5 ± 0.2	6.3 ± 0.5	1
			6.1 ± 0.3	2
	CH_3COPh	3.5 ± 0.2	7.7 ± 0.3	2
Isooctane	PhCOPh	2.5 ± 0.2	7.5 ± 0.6	1
			6.8 ± 0.4	2
	CH_8COPh	2.0 ± 0.1	13.5 ± 0.5	2

Much of the photochemistry of benzophenone, especially rate studies, depends upon the triplet lifetime of benzophenone.[6-8] The most commonly used value is that obtained by Bell and Linschitz,[3] who observed a transient absorption in the flash photolysis of benzophenone in benzene which they associated with the benzophenone triplet–triplet absorption. As these authors emphasized, the lifetime of the triplet may depend strongly on solvent purity. The only solvent they used was benzene which is relatively unreactive. Furthermore, the interpretation of the data was complicated by the presence of another species which absorbed in the same region as the benzophenone triplet and was thought to be the ketyl radical. Recently, there has been some question as to the correctness of the rate constants which they determined.[9] For these reasons, we thought it would be of value to measure the lifetime of triplet benzophenone (τ) directly from the decay of its triplet emission using the solvents of the same purity that were employed for the rate studies.

The solvents were "spectrograde," routinely distilled once through a Vigreux column, the middle cut being employed. More rigorous distillation and gas chromatographic purification did not produce solvents in which τ was appreciably longer. Emission spectra were recorded on a Farrand spectrophosphofluorimeter. The apparatus for emission lifetimes, which is very simple, was similar to that described before[10] except that the light of the exciting pulse was passed through Corning filter 7-60 for benzophenone and acetophenone and filter 7-54 for triphenylene. To minimize scatter the exciting light was collimated and the emission viewed at right angles to this. For phosphorescence measurements the emitted light was passed through filters 3-72 and 5-96 while for delayed fluorescence (*vide infra*) the filter was 5-58. The lifetimes (τ) were calculated from the formula

$$I_{\text{em}}(t_i) = \alpha \sum_{j=0}^{i} I_{\text{ex}}(t_j) \exp - \frac{(t_i - t_j)}{\tau} \qquad (1)$$

where $I_{\text{ex}}(t_j)$ and $I_{\text{em}}(t_i)$ are the intensities of the exciting flash and the emission at times t_j and t_i, and α is an arbitrary scaling factor which allows for the fact that the photomultiplier sees only a fraction of the emitted light. Typical flash energy was 2×10^{-11} einstein/pulse. Thus for a 5-ml solution of 10^{-2} M benzophenone in isooctane there is less than 0.00005% decomposition per flash. Buildup of photolysis products which could cause quenching[9] is therefore unimportant. In agreement with this, kinetic data obtained after 1 and after 20 flashes were indistinguishable.

Lifetimes determined by the emission technique are shown in Table I. Two methods were employed to determine the rate constant of triplet quenching by naphthalene: (1) direct measurement of the variation in the lifetime of the triplet as quencher (Q) is added

$$1/\tau_Q = 1/\tau + k_q[Q] \qquad (2)$$

(2) measurement of the steady-state emission intensities in the presence, I(Q), and absence, I(0), of varying concentrations of Q

$$\frac{I(0)}{I[Q]} = 1 + \tau kq[Q] \qquad (3)$$

These values agree well with those suggested by Wagner[9] but are significantly greater than those obtained by Bell and Linschitz.[3] It should be pointed out that τ is to be regarded only as an experimentally measured quantity and not as an "intrinsic" constant of triplet benzophenone in the appropriate solvent. It is always possible that at a future date a better method of purifying the solvents may be found. However, this will not affect our values of k_q.

Using triplet–triplet absorption spectroscopy, Herkstroeter and Hammond[11] have made careful studies of k_1, the first-order decay constant of aromatic hydrocarbon triplets in benzene of high purity at room tem-

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perature. Partly as a further check of the purity of our solvents and partly to form a link between this work and theirs, we determined k_1 for triphenylene using our emission apparatus to follow both the decay of the triplet emission and the decay in the delayed fluorescence.[12,13] The values obtained for k_1, 1.6×10^3 and 1.4×10^3 sec^{-1}, respectively, agree well with the published value of 1.6×10^3 sec^{-1}.[11] Thus at present we would agree with the assessment of Bell and Linschitz that it is unlikely that the short lifetime of triplet benzophenone in benzene is accounted for by impurity quenching, but rather specific interaction between solvent benzene and the triplet has to be sought. In the case of isooctane solvent the short lifetime is undoubtedly accounted for by hydrogen abstraction from the solvent. Using $1/\tau = k_a[\text{solv}]$, the rate constant for hydrogen abstraction from isooctane by triplet benzophenone (k_a) = $6.6 \times 10^4\ M^{-1}$ sec^{-1} which agrees well with other estimates.[3,14]

The above techniques allow the rate constants of interaction (k_{ir}) of a wide range of substrates (S) with triplet ketones to be determined through eq 2 and 3 with k_{ir} and S replacing k_q and Q. We have obtained data for azoalkanes, ethers, alcohols, and amines, and we shall report later on these studies.

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"Active" Sulfuration of Norbornenes

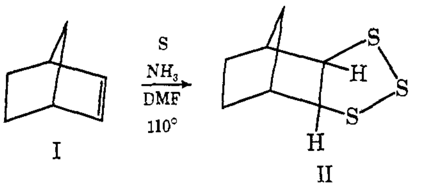
Sir:

There are many reports in the literature which describe the reaction of olefins with elemental sulfur. Temperatures of 140–180° are routinely employed and complex mixtures of polysulfides result.[1] Amines are known to enhance the reaction.[2]

We now wish to report a new reaction which results in selective and stereospecific sulfuration of certain olefins in 80–90% yields. The reaction proceeds between 90 and 110° when elemental sulfur is "activated" by ammonia in the presence of a suitable amide promotor.

Amorphous sulfur (7.5 g-atoms) slurried in 3.5 kg of dimethylformamide was treated by bubbling ammonia (0.50 mole) at 35°. Bicyclo[2.2.1]hept-2-ene (I) (4.45 moles) was added and the mixture was stirred for 2 hr at 110°. After quenching with ice water and extracting with ether, vacuum distillation afforded 2.155 moles of *exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane (II), isolated as a pale yellow oil (86% yield based on sulfur).

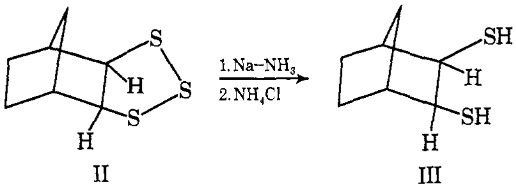
The nmr spectrum (CS_2) of II shows a complex pattern between δ 0.80 and 2.30 (6 H) with a narrow multiplet at 2.42 (2 H, norbornyl bridgehead).



I II

A doublet ($J \sim 2$ Hz) at 3.60 (2 H, sulfur geminal) indicates coupling between the bridge *anti* proton and the sulfur geminal protons in the *endo-cis* position.[3] Compound II also shows a mass spectral parent peak at *m/e* 190 and a uv absorption at $\lambda_{\max}^{C_6H_{12}}$ 284 mμ (log ε 3.576). The elemental analysis requires $C_7H_{10}S_3$.

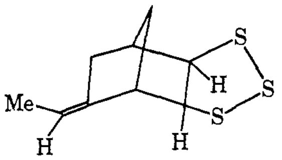
Further confirmation was obtained by sodium–ammonia reduction of II to bicyclo[2.2.1]hepta-*exo-cis*-2,3-dithiol (III) in 69% yield. The nmr spectrum (CS_2)



II III

of III possesses a complex pattern between δ 0.80 and 2.30 (10 H) containing two clear doublets ($J \sim 2$ Hz) centered at δ 1.81 (2 H, thiol); a pair of three-line patterns ($J \sim 2.2$ Hz) also appears at δ 3.15 (2 H, sulfur geminal). Simplification of the spectrum occurs when D_2O–pyridine is employed as solvent. The complex pattern between δ 0.80 and 2.30 (8 H) remains essentially unchanged except for the absence of the thiol doublets, and the protons geminal to sulfur become a doublet ($J \sim 2$ Hz) at 3.19 (2 H). The mass spectral parent peak at *m/e* 160 and elemental analysis conforming with $C_7H_{12}S_2$ further agree with the structure of III.

3,4,5-Trithianes have also been prepared in good yields from other norbornyl olefins and diolefins. For



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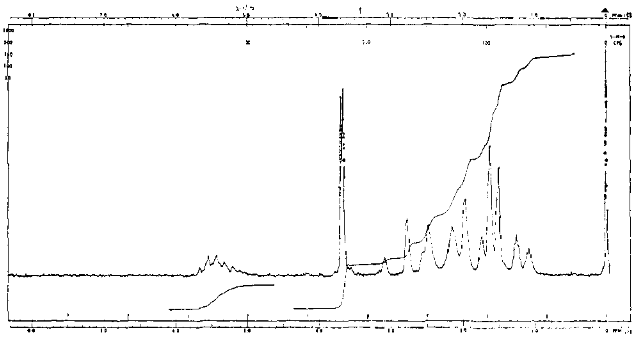

Figure 1. Nmr spectrum (60 MHz) of 8-ethylidene-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane in 50% (v/v) CS_2.

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