Table I. Proton and Carbon-13 Spectral Data for Nickel(II) Aminotroponiminates **2a**, **2b**, and the Corresponding Free Ligands

	Carbon, ppm						
	α-C	β-C	γ-C	C-1	CH_2	CH_3	CHO
			2a				
Proton isotropic shift[a]	+2.15	−1.17	−3.00			−3.95	
^{13}C shift in ligand[b]	−56.1	−79.1	−63.7	−100.1		+20.7	
^{13}C shift in complex[b]	−83.3	−65.0	−86.5	−84.2		+4.8	
^{13}C isotropic shifts	−27.2	+14.1	−22.8	+15.9		−15.9	
			2b				
Proton isotropic shift[a]	+77.2	−36.4			−146.4	−14.3	+18.8
^{13}C shift in ligand[b]	−54.6	−81.7	−72.4	−99.8	+12.7	+39.0	−136.8
^{13}C shift in complex[b]	−666.8	+594.6	*c*	*c*	−614.5	−200.8	−533.6
^{13}C isotropic shifts	−612.2	+676.3	*c*	*c*	−627.2	−239.8	−396.8

[a] Proton isotropic shifts for **2a** and **2b** were taken from ref 5b and 6, respectively; + = upfield, − = downfield. [b] Carbon-13 shifts are relative to the carbon resonance of CH_2Cl_2 used as solvent. The solutions were 0.4 *M* and, with the proton noise decoupler on the sample temperatures were about 40°. The observing frequency was 15.08 MHz. [c] Unobserved.

Table II. Predicted and Experimental Values for $\sigma_{con}{}^{C_i}/\sigma_{con}{}^{H_i}$ for the Paramagnetic Forms of the Nickel(II) Aminotroponiminates

	Ligand Position					
	α-C	β-C	γ-C	CH_2	CH_3	CHO
			Predicted[a]			
	−8.4	−18.1	−8.0			
			Experimental			
2a	−12.65	−12.05	−7.60		+4.03	
2b	−7.93	−18.58	*b*	+4.28	+16.68	−21.11
2c	−14.9	−10.5	*b*			

[a] Predicted values are the result of using the same set of $\rho_{C_i}{}^{\pi}$'s for each complex. There are only minor changes[5,6] in the experimental values between the complexes. The set used is $\rho_{C\text{-}\alpha}{}^{\pi} = +0.040$, $\rho_{\beta\text{-}C}{}^{\pi} = -0.020$, $\rho_{\gamma\text{-}C}{}^{\pi} = +0.055$, and $\rho_{C\text{-}1}{}^{\pi}$ (from ref 5b) = −0.015. [b] Unobserved.

The pattern of the experimental ratios for **2a** is the same as that previously observed[2] for **2c**, and it is important to note that for **2a** good agreement is obtained for the γ position, which was not observed for **2c**, consistent with a rapid attenuation of σ delocalization with the intervening bonds. However, the results for **2b** are markedly different from those of the other two complexes, in showing close agreement between experimental and predicted values of $\sigma_{con}{}^{C_i}/\sigma_{con}{}^{H_i}$. The complexes **2b** and **2c** exhibit proton isotropic shifts within 2 ppm for the α and β positions, but the ^{13}C isotropic shifts differ by about a factor of two. It appears, therefore, that the mechanisms of the proton and ^{13}C isotropic shifts are markedly different in these complexes, with the proton ring position being less sensitive to structural change, as witnessed by the substantial constancy of the experimental $\rho_{C_i}{}^{\pi}$ values.[5,6] Again, it appears that propagation of spin density through σ bonds can be important in determining the direction and magnitude of the ^{13}C isotropic shifts, but is probably of less importance in determining the contiguous proton shifts. In **2b**, the situation is probably complicated by the formyl group which may interact strongly with the electrons in the π framework of the cycloheptatriene ring as proposed to explain the apparent anomalous positive isotropic shifts of the formyl proton.[6]

Further evidence demonstrating the sensitivity of the ^{13}C isotropic shifts to the σ spin density is apparent from the shifts of the carbons of the *N*-alkyl substituents of **2a** and **2b**. For the CH_3 group of **2a** and the CH_2 group of **2b** $\sigma_{con}{}^{CH}/\sigma_{con}{}^{CH}$ can be written as

$$\sigma_{con}{}^{C\mathrm{H}}/\sigma_{con}{}^{\mathrm{C}H} = \frac{\gamma^{\mathrm{H}}}{\gamma^{\mathrm{C}}}\frac{a^{C\mathrm{H}}}{a^{\mathrm{C}H}} = \frac{\gamma^{\mathrm{H}}}{\gamma^{\mathrm{C}}}\frac{Q_{\mathrm{NC}}{}^{\mathrm{C}}\rho_{\mathrm{N}}{}^{\pi} + k^{\mathrm{C}}\rho_{\mathrm{C}}{}^{\sigma}}{Q_{\mathrm{NCH}}{}^{\mathrm{H}}\rho_{\mathrm{N}}{}^{\pi} + k^{\mathrm{H}}\rho_{\mathrm{H}}{}^{\sigma}} \qquad (3)$$

where $\rho_N{}^{\pi}$ is the p_{π} spin density at the nitrogen, and is positive.[5] $Q_{NC}{}^{C}$ and $Q_{NCH}{}^{H}$ are proportionality constants which are negative and positive, respectively. $\rho_C{}^{\sigma}$ and $\rho_H{}^{\sigma}$ are the σ spin densities at carbon and proton, respectively, while k^C and k^H are positive constants. Thus, the π and σ contributions to the ^{13}C isotropic shifts are of opposite sign, while they are of the same sign for the proton, consistent with the small experimental ratio. However, the σ contribution to the ^{13}C isotropic shift must be dominant, as witnessed by the observed downfield shift. Any π contribution to the shift of the CH_3 carbon in **2b** is expected to be small and σ effects appear to be dominant as judged by a fourfold increase in the ratio $\sigma_{con}{}^{CH}/\sigma_{con}{}^{CH}$ between the CH_2 and CH_3 groups. It can be seen from these results that the ^{13}C isotropic shifts of the alkyl group carbons are more sensitive to σ spin density than are the shifts of proton directly attached to the same carbon.

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Wavelength Dependence and Orbital Symmetry Controlled Sensitizer Selectivity in the Photochemistry of 2-Benzal-5-methylcyclopentanone

Sir:

A number of α,β-unsaturated carbonyl compounds undergo different photochemical reactions in solution with different wavelengths.[1] This behavior implies the existence of two or more reactive excited states which

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(1) For leading references see (a) E. F. Ullman, *Accounts Chem. Res.*, **1**, 353 (1968) and (b) E. F. Ullman and N. Baumann, *J. Amer. Chem. Soc.*, **90**, 4158 (1968); in press. (c) N. Baumann, M. Sung, and E. F. Ullman, *ibid.*, **90**, 4157 (1968).

Table I. Photostationary Isomer Ratios and Hydrogen Abstraction Quantum Yields in Isopropyl Alcohol

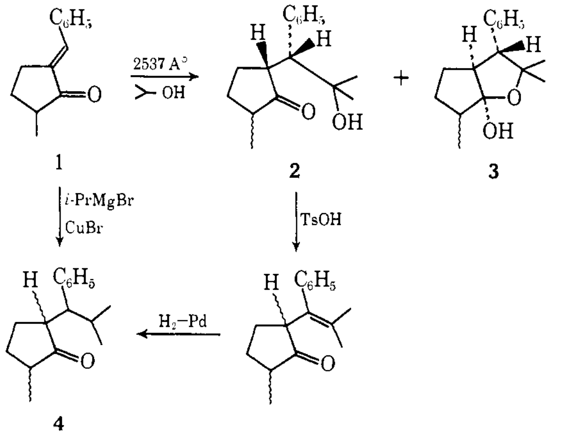
Sensitizer E_T, kcal/mol	Sensitizer	[**1**], 10^4 *M*	% trans	$\Phi^a \times 10^2$	Sensitizer selectivity[b] Found	Pred
84.0	Benzene	1.2	30	8.4	U	U
68.0	Triphenylene	1.2	44	<0.14	S	S
67.9	Fluorene	1.2	35	7.6	U	U
65.5	Biphenyl	1.2	51	1.2	U	U
61.8	Phenanthrene	1.2	30	<0.14	S	S
61.7	*o*-Terphenyl	2.1	67	0.98	U	S(?)[c]
60.9	Naphthalene	1.2	47	2.8	U	U
58.9	1-Phenylnaphthalene	3.2	81	1.3	U[d]	S
58.8	2-Phenylnaphthalene	2.2	15	<0.0014	S	S
58.4	*p*-Terphenyl	1.2	60	0.87	U	U
56.6	Chrysene	2.6	75	1.2	U	S
52.7	Fluoranthene	2.6	58	0.40	U	U
48.0	Pyrene	1.2	[e]	<0.14	[e]	U

[a] Quantum yield of hydrogen abstraction based on zero-order rates of disappearance of *trans*-**1** after the photostationary state was reached. [b] U unselective, S selective ("found" values based on rate data given in column 5). [c] Nonplanarity of *o*-terphenyl prevents face-to-face approach and invalidates prediction. [d] Dotted line probable T_2 energy. [e] Very slow reaction; E_{T_1} of **1** ~54 kcal/mol (S–T absorption under high oxygen pressure).

undergo inefficient interstate crossing. Support for two reactive triplet states in wavelength sensitive α,β-unsaturated lactones was recently obtained by the initiation of different reactions with different triplet sensitizers.[1b] We now describe the photochemistry of a related unsaturated ketone **1** which further exemplifies wavelength and sensitizer control of photochemical reactions.

Irradiation of *trans*-**1** [$\lambda_{\max}^{i\text{-PrOH}}$ 224 mμ (ϵ 2980), 227 (3100), 296 (9550), and 360 (150)] in isopropyl alcohol caused isomerization to *cis*-**1** [similar ultraviolet spectrum; nmr τ 3.35 (CH=C) shifted from carbonyl-deshielded *trans*-**1** signal under ArH multiplet, τ 2.6] without wavelength dependence ($\phi_{2537} = 0.26$, $\phi_{3650} = 0.28$). Isomerization was accompanied by disappearance of both chromophores with 2537-Å light but not with >2800-Å light ($\phi_{2537} = 0.083$, $\phi_{3650} < 0.00013$).[2] An unconjugated hydroxy ketone **2** (50%) and a nonketonic alcohol **3** (15%) were isolated. Base-catalyzed isomerization of **3** to **2** and transformation of both **1** and **2** to **4** (Chart I) permit identification of the photoproducts **2** and **3** as those expected to arise by light-induced hydrogen abstraction from isopropyl alcohol.

Chart I



Sensitization experiments were monitored by vpc. Initial rapid disappearance of *trans*-**1** due to isomerization occurred with all sensitizers. This was followed by slower zero-order disappearance of both isomers which is attributed to the hydrogen abstraction reaction. Photostationary isomer ratios during this latter stage and quantum efficiencies of the hydrogen abstraction reaction with different sensitizers are given in Table I. As in the unsaturated lactone study certain sensitizers selectively initiated only the isomerization reaction whereas others initiated both reactions unselectively.[1b] The selective sensitizers affected the photostationary isomer ratios differently than the unselective sensitizers (Figure 1). Sensitizer energies near 59 kcal/mol produced maximum trans–cis ratios with unselective sensitizers and a minimum ratio with the selective sensitizers.

Although sensitizer selectivity is not related in an obvious way to the sensitizer triplet energies, triplet energy transfer is nevertheless implicated. Beer's law dependence of solutions containing **1** plus a sensitizer eliminates possible ground-state ketone–sensitizer complexes. Singlet energy transfer cannot account for the observed reactions because of the inability of energetically accessible singlets of **1** to undergo hydrogen abstraction upon direct light excitation.[3] The sensitization data thus suggest the existence of two reactive triplet states of **1**. Selective sensitizers cause only isomerization, probably by population of a π,π^* triplet, whereas unselective sensitizers cause hydrogen abstraction which probably occurs through an n,π^* triplet.

In the sensitization of unsaturated lactones, the selective sensitizers were related by their orbital symmetry characteristics.[1b] Upon atom-for-atom comparison of spatially matched atoms in face-to-face sensitizer–acceptor complexes the signs of the coefficients of the highest filled molecular orbitals of the sensitizers exactly matched those of the lowest unfilled orbitals of the acceptors. None of the unselective sensitizers had sets of atoms in proper spatial array for perfect orbital symmetry matching. A search for similar orbital symmetry matching between **1** and the present sensitizers leads to the predictions of sensitizer selectivities given in Table I. The method successfully

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(2) The very small percentage of light absorbed by traces of acetone or other impurities is inadequate to account for this behavior.

(3) Although singlet exiplexes might undergo different chemistry than the uncomplexed excited ketones, efficient exiplex formation is precluded by the low concentrations of **1**.

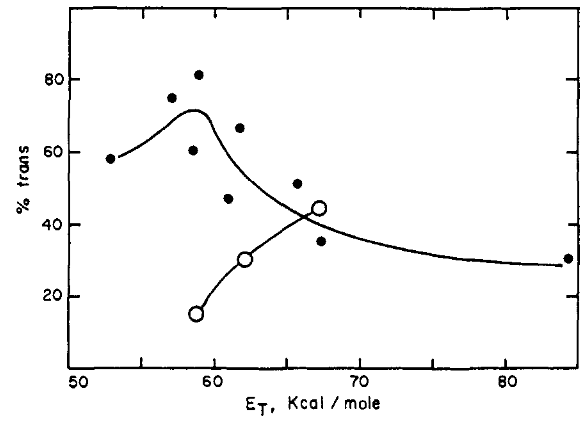

Figure 1. Photostationary states of 2-benzal-5-methylcyclopentanone (**1**) as a function of sensitizer triplet energy: ●, unselective sensitizers; O, selective sensitizers.

predicts the selectivities of sensitizers with $E_T > 59$ kcal/mol but fails to predict that all lower energy sensitizers are unselective.[4] This result is predictable if there is an isomer of **1** having a ~59-kcal/mol T_2 state with π,π^* character. Lower energy potentially selective sensitizers would then have insufficient energy to populate the T_2 state, and exothermic energy transfer would ensue causing population of the T_1–n,π^* hydrogen abstraction intermediate. The observed occurrence of isomerization even with the lower energy sensitizers could be due to competing nonvertical energy transfer to give a distorted $^3(\pi,\pi^*)$ state or to isomerization of the T_1 $^3(n,\pi^*)$ state.

The changes in the photostationary ratios on reducing the triplet energies of the sensitizers also suggest a T_2–π,π^* state of **1**. The *decrease* in the trans–cis ratio with lower energy *selective* sensitizers suggests that the cis-π,π^* triplet is more energetic than the trans-π,π^* triplet and therefore is populated less efficiently on lowering the sensitizer energies. The *increase* in the trans–cis ratio with lower energy *unselective* sensitizers implies that, conversely, with these sensitizers the efficiency of excitation to the trans-π,π^* triplet falls off faster than to the cis-π,π^* triplet. Analogy with sensitization of oxygen to its $^1\Sigma_g{}^+$ state suggests that excitation to T_2 states may fall off rapidly with sensitizers having energies up to 10 kcal/mol above the T_2 energy.[5] Thus if the π,π^* triplet of *trans*-**1** is a T_2 state, excitation to this state with unselective sensitizers could become inefficient earlier than excitation of *cis*-**1** to its higher energy T_1 π,π^* state.

(4) This is strictly true only if the nearly identical triplet energies given for the two phenylnaphthalene sensitizers are reversed.

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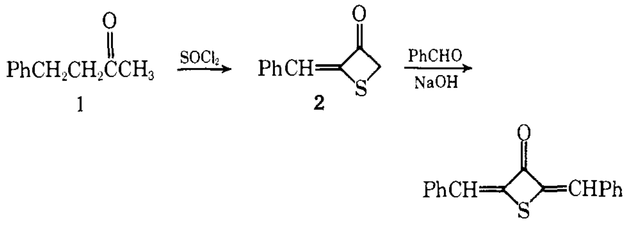
Oxidations by Thionyl Chloride. II. 3-Thietanones from Ketones

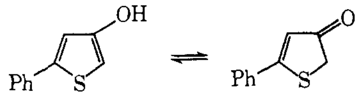
Sir:

Thionyl chloride, in the presence of catalytic amounts of pyridine, reacts abnormally with aliphatic carboxylic acids to afford α-chloro-α-chlorosulfenyl acid chlorides[1] and—with 3-arylpropanoic acids—benzo[*b*]thiophenes.[1a] Formation of the former can be rationalized mechanistically in terms of a Hell–Volhard–Zelinsky (HVZ) type addition of thionyl chloride to the enol of the carboxylic acid chloride to afford an α-sulfinyl chloride which may be converted to the sulfenyl chloride by a sequence of steps finding close analogy in the Pummerer rearrangement.[1a] The operation of this mechanism in the case of ketones might be surprising, since not only does that group appear to be inert to the action of thionyl chloride,[2] but also, if reaction did occur, a *gem*-dichloride might be expected instead.[3] During attempts to detect the operation of the HVZ- and Pummerer-type mechanisms with ketones, an unexpected cyclization occurred which led to a new one-step synthesis of a relatively unfamiliar class of compounds, the 3-thietanones.[4]

Treatment at room temperature of 4-phenyl-2-butanone, **1**, with an excess of thionyl chloride in the presence of catalytic amounts of pyridine gave rise to a vigorous, exothermic reaction which afforded 2-benzylidene-3-thietanone, **2**, 37.5%, mp 113.1–113.9°; the remaining material was intractable. The structure was established through analysis of the infrared ($\lambda_{\max}^{\text{KBr}}$ 5.75 μm), nmr (CCl$_4$, three singlets at τ 2.66, 2.78, and 5.75 in the ratio 5:1:2), and ultraviolet ($\lambda_{\max}^{\text{EtOH}}$ 361.5 (log ϵ 4.20), 292 (infl., 3.41), 265 (infl., 3.80), 242 (4.20), and 235 (infl., 4.17) nm) spectra which clearly differentiated **2** from an alternative product, 5-phenylthiophen-3-ol[10] (**3**). Base-catalyzed condensation of **2** with benzaldehyde yielded bisbenzylidene-3-thietanone, **4**, mp 168–169°. The structure of the latter was



1 **2** **4**



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