trum *m/e* (rel intensity) 163 (6), 162 (37), 147 (32), 133 (68), 119 (52), 117 (28), 115 (28), 105 (86), 95 (21), 93 (23), 91 (86), 81 (20), 79 (37), 77 (55), 69 (30), 67 (25), 65 (30), 63 (21), 55 (56), 53 (34), 51 (31), 41 (100), 39 (50); exact mass, 162.1408 (calcd for $C_{12}H_{18}$: 162.1408).

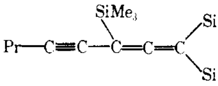
4,6-Diethyl-4,5-hexadien-7-yne (16a). ^{1}H NMR (CCl_4) δ 2.24 (m, 2 H), 1.92 (m, 6 H), 1.36 (m, 2 H), 1.20–0.72 (m, 12 H); IR (neat) 2950, 2920, 2860, 1455, 1445, 1370, 1315, 1060, 900 cm^{-1}; UV λ_{max} (cyclohexane) 222 nm (ϵ 6000); mass spectrum *m/e* (rel intensity) 190 (26), 175 (13), 162 (22), 161 (100), 147 (28), 133 (10), 131 (18), 119 (68), 117 (22), 115 (15), 107 (15), 105 (81), 93 (23), 91 (60), 79 (24), 77 (32); exact mass 190.1728 (calcd for $C_{14}H_{22}$: 190.1722).

Acknowledgment. This work was supported by the U.S. Air Force Office of Scientific Research (NC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR 74-2644.

References and Notes

(1) J. Klein and J. Y. Becker, *J. Chem. Soc., Perkin 2*, 599 (1973).

(2) Klein and Becker also examined the products from metalation followed by derivatization with trimethylchlorosilane of 2,4-octadiyne. The structure assigned to the major product was the allenyne i. The similarity of these



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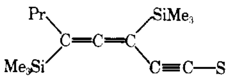

ii

reactions to those of 2,4-hexadiyne prompts us to suggest that this assignment is also in error. The chemical shift of the methylene protons at δ 1.93 indicate they are attached to an allenic carbon atom and not an acetylenic one. We propose that further investigation will show the correct structural assignment to be ii.

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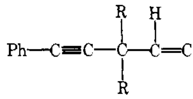
(7) The reported chemical shifts for compound **13** are all downfield by 0.35 ppm. This discrepancy can perhaps be explained by external Me_4Si being used in ref 6.

(8) This is similar to the UV spectrum of 2-methyl-2,3-heptadien-5-yne (λ_{max} 220 nm in hexane); L. Skatteb⌀l, *Tetrahedron Lett.*, 2175 (1965).

(9) Similarly, J. Klein, S. Brenner, and A. Medlik, *Isr. J. Chem.*, **9**, 177 (1971), have shown that the dilithiated derivative of 5-phenyl-1-penten-4-yne reacts with alkyl halides to give exclusive formation of the unconjugated enyne iii while reaction with trimethylchlorosilane resulted in conjugated allenes as the major products, i.e., iv:



$$Ph{-}C{\equiv}C{-}CR_2{-}CH{=}CH_2$$

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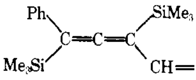

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Photochemistry of Organochalcogen Compounds. 3. Photochemistry of Bis(benzoylmethyl)tellurium Dichloride

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Contribution from the Xerox Corporation, Webster Research Center, Webster, New York 14580. *Received May 31, 1975*

Abstract: The photochemical β-cleavage and Norrish type II reactions for bis(benzoylmethyl)tellurium dichloride (**1**) have been investigated. No room temperature emission is observed for **1**, but at 77 K in methyltetrahydrofuran glass, phosphorescence is detected with quantum yield $\phi_p = 0.18$ and lifetime $\tau_p = 24$ ms. The spectroscopic triplet state is assigned as originating principally from a $^3\pi,\pi^*$ state with appreciable $^3n,\pi^*$ character. Photolyses of **1** with 313 nm light in degassed fluid solutions at 298 K result in the formation of acetophenone, chloroacetophenone, and tellurium metal as the principal photoproducts. In H atom donating solvents, the quantum yield of acetophenone produced may exceed 2, while chloroacetophenone is formed only in trace amounts. In inert solvents, chloroacetophenone and tellurium are formed in major amounts with lesser amounts of acetophenone and trace amounts of dibenzoylethane also produced. The formation of acetophenone and chloroacetophenone *cannot* be quenched with normal triplet quenchers but the triplet state of **1** can be sensitized with xanthene-9-one. These results suggest that β-cleavage and Norrish type II processes may occur from a very short-lived $^3\pi,\pi^*$ state probably identical with the spectroscopically observed triplet state.

Introduction

The photodecomposition of organic selenium and tellurium compounds has been known for over a century,[1,2] and quite often these photoreactions are accompanied by formation of elemental selenium and tellurium. Not all organochalcogen compounds are unstable, for example, the carbon–tellurium bond in diaryl tellurium dihalides is generally quite stable.[3] In spite of the interesting differences in photochemical behavior of organochalcogen compounds, the literature contains scant molecular structure-property relationships, and no detailed photochemical studies have been reported until quite recently. Chu, Marsh, and Günther[4] have reported details of the photochemistry of benzyl diselenide in which photolytic C–Se bond scissions and subsequent free-radical processes are responsible for the formation of elemental selenium and other observed photoproducts.

A recent patent[5] has disclosed the photo- and thermal decomposition of bis(benzoylmethyl)tellurium dichloride (**1**), and some preliminary results of the photochemistry have been presented.[6] We wish to report here some details of the photochemical, photophysical, and thermal behavior of this compound.

Experimental Section

Experimental Apparatus. Ultraviolet and visible electronic absorption spectra were determined with a Cary 15 spectrophotometer, mass spectral analyses with a Hitachi Perkin-Elmer RMU-6E mass spectrometer, and infrared spectra using a Perkin-Elmer Model 267 spectrophotometer. NMR spectra were determined on a JEOL C60H spectrometer with $CDCl_3$ or CD_3CN as solvents and Me_4Si as an internal standard. GLC analyses were carried out on a Hewlett-Packard 5750 research chromatograph using a 6 ft × ⅛ in. stainless steel column with 10% Carbowax 20M on Chromosorb P AWDMCS 60/80 mesh support and temperature programming. Emission spectra were obtained on a research spectrofluorophosphorimeter constructed in this laboratory. In this apparatus, excitation light from a 500-W Xenon arc is collimated and focused onto the entrance slit of a Jarrell-Ash 0.25-m Ebert grating excitation monochromator to provide monochromatic light (16 Å/mm dispersion). Sample emission is monitored at right angles to the exciting light with a MacPherson 0.3-m grating monochromator and an RCA 7265 photomultiplier tube.

A quartz immersion apparatus equipped with a cold-water cooling jacket and the Pyrex filtered output of a 450-W Hanovia medium-pressure mercury arc was used for preparative scale photochemical reactions. All irradiations were performed on deoxygenated solutions under a nitrogen blanket.

For quantum yield determinations, solutions were irradiated with the collimated outputs of a PEK 112 high-pressure mercury arc or an Osram 100 W/2 super pressure mercury arc. The light was filtered through 5 cm of cold water to prevent sample heating, then through Corning glass filters to isolate 313 nm light. Actinometry was determined using a 16 junction, circular, Eppley thermopile and Keithley Model 150A microvoltammeter previously calibrated with the potassium ferrioxalate chemical actinometer.[7]

Materials. Bis(benzoylmethyl)tellurium dichloride, (**1**) was prepared by a modification of a procedure described by Rust,[8] in which the reaction of tellurium tetrachloride with acetophenone in anhydrous alcohol free chloroform in the dark at 24 °C yields **1** (60%): mp 190 °C dec; IR ($CHCl_3$) 1660 cm^{-1} (C=O); NMR ($CDCl_3$) δ 5.45 (4 H, S, CH_2), 7.55-8.26 (10 H, m, aromatic). Analysis[9] calculated for $C_{16}H_{14}Cl_2O_2Te$: C, 43.99; H, 3.32; Cl, 16.23; Te, 29.21. Found: C, 43.81; H, 3.17; Cl, 16.14; Te, 29.33. Acetophenone and chloroacetophenone were obtained from Aldrich Chemical Co., Inc. 1,2-Dibenzoylethane was synthesized according to the procedure of Lutz, Love, and Palmer.[10] The crude material was recrystallized from ethanol to yield crystalline needles (61%), mp 144-145 °C (lit.[11] 144-145 °C). The purity and structure of **1** were confirmed by thin-layer chromatography (TLC), differential scanning calorimetry (DSC), melting point, NMR, IR, and UV spectra. A single spot TLC and a sharp melting curve in DSC measurement indicate the high purity of **1**.

Results and Discussion

Spectroscopic Triplet State. The ultraviolet electronic absorption spectrum and phosphorescence emission spectrum for **1** are shown in Figure 1. The absorption spectrum in methyltetrahydrofuran solvent has maxima at 255 nm (40 000 M^{-1} cm^{-1}), 285 nm (2800 M^{-1} cm^{-1}), and near 325 nm (50 M^{-1} cm^{-1}), which is similar to the absorption spectrum for acetophenone in cyclohexane which has bands at 240 nm (13 000 M^{-1} cm^{-1}), 285 nm (1000 M^{-1} cm^{-1}), and near 325 nm (50 M^{-1} cm^{-1}). The lowest energy band for **1** has been assigned as an ${}^1n,\pi^*$.

No room-temperature emissions have been observed for **1** in dilute fluid solutions; however, at 77 K in MTHF rigid glass **1** exhibits phosphorescence with a 0-0 band at 396 nm, a quantum efficiency of 0.18, and an observed lifetime of 24 ms, a lifetime which is rather long for a ${}^3n,\pi^*$ state and too short for a ${}^3\pi,\pi^*$ state.

The nature of the emitting triplet state in acetophenone has recently been discussed.[12] In the vapor phase, the emitting triplet has definitely been assigned as a ${}^3A''$ (n,π^*).[13,14] The energy gap for the zero-point levels of the ${}^3n,\pi^*$ and ${}^3\pi,\pi^*$ states is estimated to be 700-800 cm^{-1} in the vapor phase. Li and Lim[15] proposed for acetophenone a ${}^3\pi,\pi^*$ emitting level based upon emission polarization experiments at 77 K in EPA glass. The ${}^3\pi,\pi^* \rightarrow S_0$ transition actually obtains ${}^3n,\pi^* \rightarrow S_0$ polarization due to the strong coupling of the nearby triplet levels. Upon going from the vapor state to *n*-pentane or methyl benzoate matrix at 4.2 K, a narrowing of the energy gap between the ${}^3n,\pi^*$ and ${}^3\pi,\pi^*$ states is expected, resulting in about 100-200 cm^{-1} between zero-point levels. The result of low-frequency $COCH_3$ torsional modes in the excited states should allow the environmental perturbation to strongly couple ${}^3n,\pi^*$ and ${}^3\pi,\pi^*$ states.[14] In fact, the strong coupling at 4.2 K results in multiminimal energy surfaces and dual phosphorescence with lifetimes of 4 ms (${}^3n,\pi^*$) and 80 ms (${}^3\pi,\pi^*$). The results of varying temperature and environment are to alter the nature of the emitting triplet state for acetophenone, due to very strong coupling of near-by states.

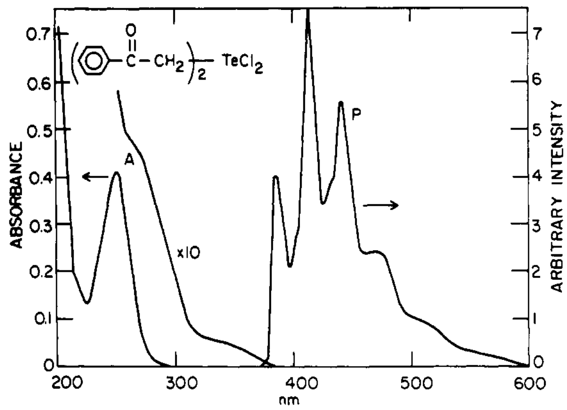

Figure 1. The electronic absorption spectrum, A, for 10^{-4} M bis(benzoylmethyl)tellurium dichloride in methyltetrahydrofuran at 298 K, and the phosphorescence spectrum, P, at 77 K.

Such effects no doubt are present in **1**; the anomalous observed lifetime for the triplet state is entirely consistent with an emitting ${}^3\pi,\pi^*$ state with appreciable ${}^3n,\pi^*$ character due to strong mixing of near-by triplet levels. The tellurium atom is expected to enhance the low-frequency torsional modes, thereby permitting environmental perturbations to mix the two triplet levels. In addition, the presence of tellurium should provide an internal heavy atom effect[16] and perturb intercombinational transitions in **1**. Thus, the anomalous lifetime in **1** is also consistent with a ${}^3\pi,\pi^*$ state whose lifetime is shortened by such an internal spin-orbit effect.

Photochemistry in Solution. Bis(benzoylmethyl)tellurium dichloride (**1**) undergoes facile photochemical β cleavage of carbon-tellurium bonds and an intramolecular Norrish type II photoelimination reaction as the sole photochemical processes. In this respect, the photoreactions of **1** are similar to photoreactions reported for β-sulfinylacetophenone[17] in which type II and β cleavage occur, for α-alkoxyacetophenones[18] which exhibit type II processes, and for benzoin phenyl ether,[19] α-phenoxyacetophenone,[20] and desyl sulfides,[21] all of which exhibit β-cleavage reactions.

All of these compounds contain group 5A atoms in the β position which may result in β cleavage and competing type II processes if γ-hydrogen atoms are present. The β-cleavage reaction in **1** leads to phenacyl radicals which abstract hydrogen or chlorine atoms in subsequent free radical reactions to form acetophenone and chloroacetophenone, respectively. The type II process leads to acetophenone in an intramolecular concerted process.

Tellurium metal and acetophenone are the two major photoproducts formed during photolyses of **1** at 313 nm in de-

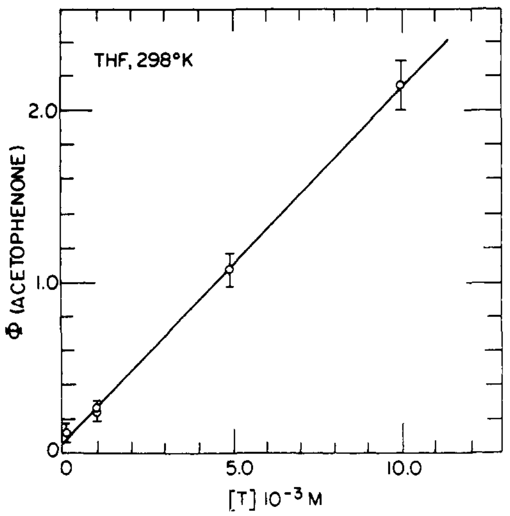

Figure 2. The quantum yield of acetophenone formation from bis(benzoylmethyl)tellurium dichloride in degassed tetrahydrofuran at 298 K, plotted against initial concentration. The value at 10^{-2} M is an average of two experiments (Table I).

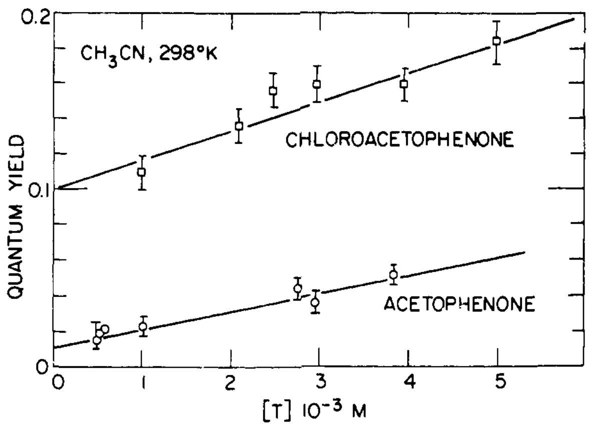

Figure 3. The quantum yield of acetophenone (○) and chloroacetophenone (□) formation from bis(benzoylmethyl)tellurium dichloride in degassed benzene and acetonitrile solutions at 298 K.

Table I. Quantum Yields[a] for Formation of Acetophenone and Chloroacetophenone

No.	Bis(benzoyl-methyl)-tellurium dichloride	Solvent	Φ_A	Φ_{ClA}
1	0.1	THF	0.13	
2	1.0	THF	0.23	
3	1.0	THF	0.26	
4	5.0	THF	1.08	
5	10.0	THF	1.99	
6	10.0	THF	2.33	
7	0.52	C_6F_6	0.015	
8	0.57	C_6F_6	0.019	
9	0.61	C_6F_6	0.021	
10	1.04	CH_3CN	0.023	0.108
11	2.13	CH_3CN		0.135
12	2.50	CH_3CN		0.156
13	2.78	CH_3CN	0.044	
14	2.96	CH_3CN	0.036	0.157
15	3.82	CH_3CN	0.051	
16	3.97	CH_3CN		0.158
17	5.0	CH_3CN		0.183
18[b]	0.5	CH_3CN	0.016	
19[b]	1.0	CH_3CN	0.034	
20[b]	2.5	CH_3CN	0.064	
21[b]	4.0	CH_3CN	0.100	
22[b]	5.0	CH_3CN	0.142	

[a] All photolyses at 298 K; quantum yields accurate to ±10%. [b] 10^{-2} M xanthen-9-one sensitizer used.

gassed hydrogen atom donating solvents. Trace amounts of chloroacetophenone and 2-phenacyltetrahydrofuran (THF solvent) have also been identified by GLC analyses. The formation of 2-phenacyltetrahydrofuran has been verified by mass spectral peaks with *m/e* values of 190, 105, 71, and 42. The parent ion is 190, the furan moiety yields a fragment with *m/e* of 71, a $COCH_2\cdot$ fragment has a value of 42, and the C_6H_6CO gives a fragment with *m/e* of 105.

Figure 2 shows the quantum yield for acetophenone formation from **1** in degassed THF solution. Error bars reflect quantum yields accurate to ±10%, the point at 10^{-2} M is the average of two determinations. The quantum yield of acetophenone is dependent upon the initial concentration of **1** and may exceed 2. The intercept in Figure 2 is about 0.01, which corresponds to the yield of acetophenone produced in an intramolecular type II process which is independent of the concentration of **1**. Quantum yields greater than 2 may be explained by a radical chain process (vide infra).

Photolyses of **1** in degassed solutions of benzene, perfluorobenzene, or acetonitrile with 313 nm light yield tellurium and chloroacetophenone as principal photoproducts. In addition, smaller amounts of 1,2-dibenzoylethane and acetophenone are produced. This may be compared with results in hydrogen atom donating solvents in which acetophenone is the major organic photoproduct. This behavior is similar to that reported for β-sulfinylacetophenone.[17] There are no observed photoreactions of acetophenone under the reaction conditions employed; however, chloroacetophenone is photosensitive after extended photolysis, and therefore photolyses of **1** were carried out to low conversions to prevent unwanted secondary photochemistry.

In Table I and Figure 3 are shown results for photolyses of **1** in degassed acetonitrile and benzene solutions at room temperature. Quantum yields for acetophenone are less than for chloroacetophenone (Figure 3), and the extrapolated minimum quantum yields for acetophenone and chloroacetophenone are 0.01 and 0.1, respectively. These extrapolated values correspond to non-free-radical processes that are independent of the concentration of **1**.

Nature of the Reactive Triplet. Of considerable interest is the observation that the formation of acetophenone and chloroacetophenone *cannot* be quenched by molecules with triplet states lower in energy than **1** (E_T = 72 kcal). For example, naphthalene (E_T = 61 kcal) and fluorene (E_T = 68 kcal) at concentrations between 2×10^{-3} M to 10^{-4} M did not affect the photochemistry of 10^{-3} M solutions of **1**. Naphthalene is known to be a good quencher of $^3n,\pi^*$ states of alkyl phenyl ketones,[22,23] for example naphthalene at 10^{-4} M concentration, has been reported to quench >30% of the product formation in deoxybenzoin.[22] At 2×10^{-3} M concentrations *some* quenching of **1** should have been observed if quenching is taking place. Additional quenching experiments were attempted using 10^{-3} M concentrations of diene quencher molecules. When *trans*-stilbene was used no cis isomer formed, and the quantum yield for acetophenone actually increased at the expense of the quantum yield for chloroacetophenone which decreased. A similar result was observed when 2,5-dimethyl-2,4-hexadiene was used. These results suggest that whereas no energy-transfer quenching has occurred, free radical reactions occur between the dienes and the radical fragments produced by β-scission processes in **1**.

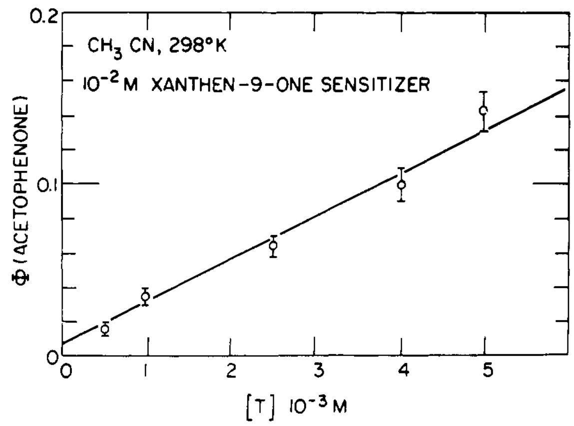

Figure 4. The quantum yield of acetophenone formation from bis(benzoylmethyl)tellurium dichloride sensitized by 10^{-2} M xanthene-9-one in degassed acetonitrile at 298 K.

Further evidence for the lack of triplet quenching in **1** was found. Under normal circumstances care is taken to exclude oxygen to prevent quenching of a ketonic triplet state.[24,25] Irradiation of **1** in air saturated solutions results in greater quantum yields for product formation as compared with deoxygenated solutions. This behavior is similar to that reported for 4-methyl-1-phenylpentan-1-one[26] for which oxygen does not quench the ketonic triplet state, and the yields of products are increased.

In spite of the fact that the triplet state of **1** cannot be quenched, it can be sensitized by xanthene-9-one ($E_T = 74$ kcal) (Table I). In Figure 4 are shown results of the sensitized photochemistry of **1** in degassed acetonitrile at room temperature. In these experiments the xanthene-9-one concentration was held constant at 10^{-2} M while the concentration of **1** was varied. The quantum yield of acetophenone formation increases linearly and has an extrapolated minimum value of $\cong 0.01$ for low concentrations of **1**. At low concentrations of **1**, $<10^{-3}$ M, the quantum yields for direct and sensitized photochemistry are equal within experimental error.

In order to investigate further possible quenching of the triplet state of **1** and to determine the triplet state lifetime in solution, attempts were made to observe room temperature fluorescence or phosphorescence, in highly purified carbon tetrachloride.[27] No room temperature emissions can be observed for **1** using the purified CCl_4 solvent under conditions for which the delayed fluorescence and phosphorescence of benzophenone are easily seen.[28] ·

The absence of room-temperature phosphorescence, together with the quenching and sensitization results, suggest that β-cleavage and intramolecular type II reactions in **1** proceed through a short-lived excited state that may be a singlet or a triplet state, or both of these states, with a lifetime $\tau \leqq 10^{-8}$ s based upon the diffusion-controlled limit of quenching for naphthalene (10^{-10} s).[22]

The lack of quenching of photoreactions for α-methylene ketones by *cis*-pyperylene and 2,3-dimethyl-1,3-butadiene and the inability to sensitize with propiophenone led Cormier and Agosta[29] to conclude that excited singlet species are responsible for the observed photoreactions. Also, based on the lack of quenching of the photocleavage of benzoin ethers by naphthalene and 1,3-pentadiene, Heine[30] has suggested that the reaction may occur via the excited singlet state. Pappas and Chattopadhyay,[31] on the other hand, based on sensitization studies of benzoin ethers with *m*-methoxyacetophenone suggest that triplet states are responsible, and the triplet lifetimes are less than 10^{-10} s, which they attribute to facile α cleavage.

The lack of quenching of β-cleavage and type II photoreactions in **1**, together with the sensitization of **1** with xanthene-9-one resulting in quantum efficiencies for β-cleavage and type II reactions equal to those observed for direct irradiation suggest that the excited triplet state is responsible for the observed photoreactions in **1**. If the rate of intersystem crossing in **1** is similar to 5×10^{-10} s^{-1} reported for benzophenone,[32] *singlet* β-cleavage reactions would require $k_\beta > 10^{11}$ s^{-1}. The rates for triplet β cleavage, k_β, and type II elimination, k_γ, in **1** must be $\geqq 10^8$ s^{-1} in order to compete with diffusion-controlled quenching. This value of k_γ in **1** is not inconsistent with results for α-alkoxyacetophenone, for which Lewis and Turro[18] report $k_\gamma \geq 10^9$ s^{-1}.

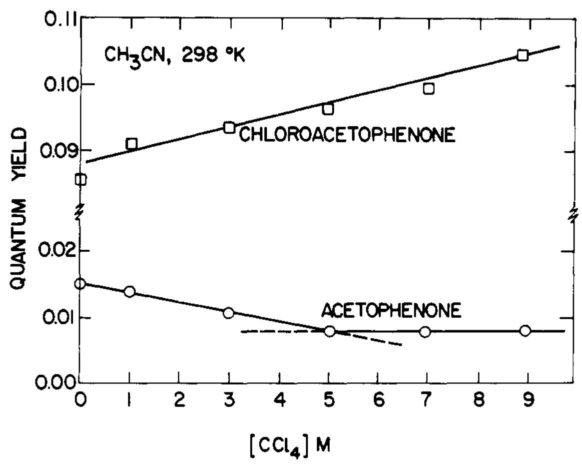

Figure 5. The quantum yield of acetophenone, (○) and chloroacetophenone, (□) formation from bis(benzoylmethyl)tellurium dichloride in degassed acetonitrile at 298 K as a function of added CCl_4 radical trapping agent.

Free Radical Trapping. Bis(benzoylmethyl)tellurium dichloride (**1**) has been shown to be an efficient photoinitiator for free radical polymerizations of methyl methacrylate under conditions that rigorously exclude ionic processes.[33] There are several lines of evidence for the intermediacy of phenacyl radicals formed during the photolysis of **1**. 2-Phenacyltetrahydrofuran, a product formed during photolyses of **1** in THF, may result from the combination of phenacyl and tetrahydrofuryl radicals. The tetrahydrofuryl radicals are formed as a consequence of phenacyl radical abstraction of hydrogen atoms from THF. In poor hydrogen atom donating solvents, 1,2-dibenzoylethane is formed presumably via combination of two phenacyl radicals. This reaction is favored in these solvents because the competing reaction of hydrogen atom abstraction from solvent by phenacyl radicals is eliminated. In addition to acetophenone produced in a concerted type II process, it may be produced as a result of hydrogen atom abstraction by phenacyl radicals from **1** or solvent. Chloroacetophenone also may be produced by chlorine atom abstraction by phenacyl radicals from **1** or other chlorine atom containing compounds, for example, carbon tetrachloride.

In order to trap free radical species formed during photolyses of **1**, experiments were attempted using dodecanethiol, a known efficient scavenger for free radicals.[19,22,34] Unfortunately the dodecanethiol reacts with ground state **1**, as do alcohols, and this precluded using this radical trap.

Carbon tetrachloride is also a useful radical trap,[35] and since **1** is completely stable in CCl_4 solution radical-trapping experiments were performed, and the results are shown in Figure 5. For increasing concentrations of CCl_4 (>1 M), the quantum yield of chloroacetophenone increases, whereas the quantum yield of acetophenone decreases to a limiting value of $\simeq 0.01$ and remains constant at that value for CCl_4 concentrations >5 M. This behavior is consistent with phenacyl radicals abstracting chlorine atoms from CCl_4 to form chloroacetophe-

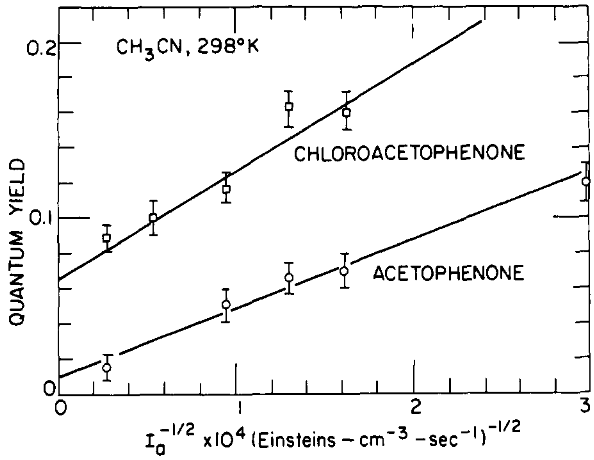

Figure 6. The quantum yield of acetophenone, (○) and chloroacetophenone (□) from bis(benzoylmethyl)tellurium dichloride in degassed acetonitrile at 298 K as a function of inverse square root of absorbed light. The points at 1.31 × 10^4 $I_a^{-1/2}$ are the average of two experiments (Table II).

none at the expense of acetophenone formation. The limiting quantum yield for acetophenone corresponds to type II photoelimination presumably through a 1,4-biradical intermediate that cannot be trapped by CCl$_4$. Wagner et al.[36] have reported mercaptan trapping of the biradical intermediates in type II photoelimination reactions of γ-methoxybutyrophenone. However in view of the fact that CCl$_4$ is perhaps three orders of magnitude less efficient than thiols as a radical trap, it seems unlikely that CCl$_4$ can intercept the 1,4-biradical intermediate in **1**.[37]

The diene quenching results for **1**, in which the quantum yield for acetophenone increases while the quantum yield for chloroacetophenone decreases, are also consistent with hydrogen atom abstraction by phenacyl radicals to produce acetophenone. 2,5-Dimethyl-2,4-hexadiene has been reported by Pryor[37] to be unreactive toward methyl radical addition reactions relative to hydrogen abstraction processes. The extrapolated quantum yields in Figures 2–5 correspond to processes for formation of acetophenone and chloroacetophenone that do not depend upon phenacyl radical attack on solvent or **1**. For acetophenone, this is the type II intramolecular photoelimination reaction. Chloroacetophenone formation may occur in a cage process prior to diffusion apart of phenacyl radicals which subsequently abstract hydrogen atoms, combine, or are scavenged by radical traps.

A Simple Reaction Mechanism. The following set of reactions and rate constants satisfactorily account for the products formed and quantum yield data for direct photolyses of **1**:

$T \rightarrow {}^1T^*$	I_a	(1)
${}^1T^* \rightarrow {}^3T^*$	k_{isc}	(2)
${}^3T^* \rightarrow T$	k_d	(3)
${}^3T^* \rightarrow A + Y$	k_γ	(4)
${}^3T^* \rightarrow 2A\cdot + TeCl_2$	k_β	(5)
${}^3T^* \rightarrow 2ClA + Te^0$	k_β'	(6)
$A\cdot + S \rightarrow A + S\cdot$	k_1	(7)
$A\cdot + T \rightarrow A + A\cdot + Y$	k_2	(8)
$A\cdot + T \rightarrow 2ClA + A\cdot + Te^0$	k_3	(9)
$A\cdot + S\cdot \rightarrow A - S$	k_4	(10)
$A\cdot + A\cdot \rightarrow A_2$	k_5	(11)
$2TeCl_2 \rightarrow TeCl_4 + Te^0$	k_6	(12)

Step 1 corresponds to excitation of **1** into the ${}^1n,\pi^*$ state. Intersystem crossing (isc) to an excited triplet state is shown in step 2. This state is probably a ${}^3\pi,\pi^*$ state with appreciable ${}^3n,\pi^*$ character similar to the spectroscopic triplet state observed at 77 K. This assignment is partially supported by the lack of products expected from intermolecular photoreduction for which ${}^3\pi,\pi^*$ states are less reactive than n,π^* states, or unreactive,[24,38-40] and by the small quantum yields for type II processes in **1** as compared with these processes from ${}^3n,\pi^*$ states for which Wagner et al.,[36,41] have reported γ-hydrogen abstraction with nearly 100% efficiency. Deactivation of the triplet state is shown in step 3 and a type II process leading to acetophenone, A, in step 4. The fragment Y formed in step 4 may be a tellurium ylide which is expected to be quite unstable[42,43] and has not been isolated as a reaction product in our photolyses. A β-cleavage process from the triplet state of **1** yields a phenacyl radical, A·, and an organotellurium radical fragment. This fragment may decompose to yield TeCl$_2$ and A·. The overall process is shown in step 5. This simplification does not alter the general form of the kinetic expression derived (vide infra). The phenacyl radicals A· may diffuse away from the cage or alternatively may react in the cage to form chloroacetophenone and Te^0 metal. This process is shown in step 6 and corresponds to chloroacetophenone production that cannot be trapped by radical scavengers. Steps 7–10 represent secondary free radical reactions of phenyl radicals A·. Step 7 shows H atom abstraction from solvent to produce acetophenone. Steps 8 and 9 show H atom and Cl atom abstraction from **1** to produce acetophenone and chloroacetophenone, respectively, and represent overall reactions similar to step 5 discussed above. The radical fragments formed initially in steps 8 and 9 are expected to be unstable and decompose to yield the overall reactions shown.[2] In good H atom donating solvents, a reaction such as that shown in step 10 is expected to occur, and the formation of 2-phenacyltetrahydrofuran in THF solvent is an example. In poor H atom donating solvents, phenacyl radical combinations can occur to form 1,2-dibenzoylethane illustrated in step 11. The disproportionation of TeCl$_4$ shown in step 12 is a known reaction.[2] The reactions shown in steps 8 and 9 form the basis for a radical chain mechanism and together with step 7 may account for the quantum yields greater than 2 observed in THF.

Using steady-state approximations for excited states and radicals the following expression for quantum yield of acetophenone in good H atom donating solvents may be derived:

$$\Phi_A = \frac{k_\gamma + k_\beta}{K} + \frac{k_\beta k_2 [T]}{k_S K}$$

in which $K = k_d + k_\gamma + k_\beta + k_\beta'$ and $k_S = k_1 [S]$. The form of this expression predicts the linear relationship between Φ_A and [T] shown in Figure 2.

The kinetic expressions for quantum yields of acetophenone and chloroacetophenone in poor H atom donating solvents are:

$$\Phi_A = \frac{k_\gamma}{K} + \frac{k_2[T]}{I_a^{1/2}} \left(\frac{k_\beta}{k_5 K}\right)^{1/2}$$

$$\Phi_{ClA} = \frac{2k_\beta'}{K} + \frac{2k_3[T]}{I_a^{1/2}} \left(\frac{k_\beta}{k_5 K}\right)^{1/2}$$

The linear dependence of Φ_A and Φ_{ClA} upon the initial concentration of **1**, [T], is shown in Figure 3. Of considerable significance is the inverse square root of absorbed light dependence for Φ_A and Φ_{ClA} predicted by these expressions. This dependence is shown in Figure 6 and Table II. These results, together with the data presented in Figure 3 (Table I), and quenching, sensitization, and radical trapping experiments verify the simple mechanism proposed. The ratios of intercepts in Figures 3 and 6 suggest that $k_\gamma = (0.25 \pm 0.05)k_\beta'$, or that

Table II. Quantum Yields[a] for Formation of Acetophenone and Chloroacetophenone

No.	I_a einstein cm^{-3} s^{-1}	$I_a^{-1/2}$	Φ_A	Φ_{ClA}
1	13.5×10^{-8}	0.27×10^4	0.015	0.086
2	3.4×10^{-8}	0.54×10^4		0.100
3	1.1×10^{-8}	0.95×10^4	0.051	0.116
4	5.86×10^{-9}	1.31×10^4	0.063	0.165
5	5.86×10^{-9}	1.31×10^4	0.070	0.159
6	3.86×10^{-9}	1.62×10^4	0.069	0.159
7	1.08×10^{-9}	3.0×10^4	0.12	

[a] 1.01×10^{-2} M **1** in acetonitrile. Photolysis done at 298 K using neutral density filters to vary the incident light intensity. Quantum yields accurate to ±15%.

the type II process is about 25% as efficient as the β-cleavage process, leading to concerted production of chloroacetophenone.

Bis(alkyl)tellurium dichlorides are known to exist in a trigonal-bipyramid structure with some tendency for distortion toward a tetrahedral structure due to interactions of the organic ligands.[44] This should allow type II processes to occur; however, the two chlorine atoms are bound to have a steric influence on the process, and this may account for its low efficiency.

Summary

The photochemistry of **1** may be summarized as involving $^3\pi,\pi^*$ state processes leading to the formation of Te^0, chloroacetophonone, and acetophenone in concerted steps. In addition, phenacyl radicals are produced which abstract from good hydrogen atom donating solvents to produce acetophenone efficiently. In inert solvents, the phenacyl radicals formed react with **1** to abstract both chlorine and hydrogen atoms and combine to form 1,2-dibenzoylethane. Tellurium may be accounted for by disproportionation of $TeCl_2$ in solution at room temperature,[2] or it may be formed directly in concerted photochemical steps. Trace amounts of other products are formed in subsequent free radical reactions.

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