lization until no impurities could be detected by thin-layer chromatography. 7*H*-Benz[*de*]anthracene-7-one (benzanthrone) was an Eastman practical chemical and was recrystallized three times from ethanol. Benzene was Mallinckrodt Nanograde and was used as received, as was mixed tritolyl phosphates, an Eastman organic chemical. Chlorobenzene, bromobenzene, and iodobenzene were Eastman reagent grade chemicals and were vacuum distilled immediately prior to use.

Procedures. All measurements of the conversion of the dyes to their less-stable geometric isomers were carried out on a flash photoelectric apparatus. Two xenon flash lamps (Kemlite Z8H2O) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose inside walls were coated with highly reflective paint (Eastman White Reflectance Coating). The flash-discharge energies were 225, 156, and 100 J, corresponding to a 2-μF capacitor charged to 15, 12.5, and 10 kV, respectively. It was determined that the light intensities of the flash discharges varied linearly with respect to the discharge energy over this range of operation and that for a given voltage charge on the capacitor, the flash intensity was reproducible to within $\pm 2\%$. Glass color filters (Corning 3391 or 3-74) were placed between the flash lamps and the sample cell holder so as to insure only visible excitation of the dyes. The monitoring source was a quartz-halide 100-W lamp (Osram 64625) powered by a regulated dc power supply (Sorensen QSB12-8). The lamp was mounted in an appropriate housing on an optical bench in series with a collimating lens, the flash chamber, a focusing lens, and a ¼-m monochromator (Jarrell-Ash). The monitoring beam, after passing through the sample cell, was focused on the entrance slit of the monochromator. Light intensity as a function of time was measured by means of a photomultiplier tube (RCA 4463) located at the exit slit of the monochromator. The output from the photomultiplier was fed into a cathode-follower amplifier and then into a wide-band digital storage oscilloscope (Nicolet Model 1090). The output voltage of the photomultiplier, read directly in digital form on the oscilloscope screen as a function of time, was linear with regard to the light intensity transmitted by the sample, so that an observed change in voltage following flash excitation could be readily converted mathematically to a change in absorbance in the sample.

The cylindrical Pyrex-glass sample cells were 25 cm long and 15 mm o.d. with flat windows fused to the ends. The cells were connected by side arms to bulbs, where solutions were contained during the degassing procedure. Solutions were degassed by subjecting them to several freeze-pump-thaw cycles on a high-vacuum manifold prior to sealing the sample containers.

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Thione Photochemistry. Intramolecular Cyclization of Aralkyl Thiones from S_2[1]

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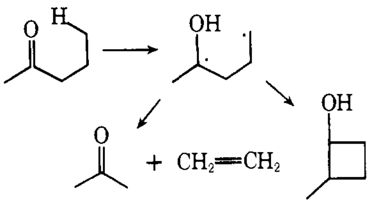
Abstract: Excitation of a series of aralkyl thiones into the S_2 (π,π^*) state leads to a formal insertion into the δ position and the formation of cyclopentyl thiols. Excitation into the S_1 (n,π^*) state does not lead to the same products and reaction is very slow. The former reaction may be quenched with biacetyl, but not with up to 2 M piperylene, nor can it be induced with a variety of triplet sensitizers. These and other observations make it probable that S_2 is the reactive state. The reaction may thus be (π,π^*) fast hydrogen abstraction or a concerted $2_\pi + 2_\sigma$ process. Use of a thione with a chiral center in the γ position results in racemization of starting material following excitation into S_1, but not into S_2. With a thione possessing a δ chiral center recovered starting thione is, following S_2 excitation, unracemized.

Intramolecular hydrogen abstraction in excited carbonyl compounds is among the more extensively studied of photic reactions. This transformation, which occurs both in aliphatic and aralkyl substances, was originally reported by Norrish nearly forty years ago.[2a] He then described the cleavage, since termed the (Norrish) type II, which occurs between the β and

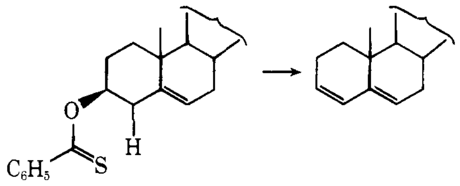
γ carbon atoms of such compounds. Later,[2b] Yang reported the frequently accompanying reaction: the formation of cyclobutanols. The reaction has been shown to proceed via



biradicals and originate from the n,π^* states. In aromatic substances only the triplet is concerned, but in aliphatic compounds the participation of the singlet has been demonstrated.[3] Further, an additional "invisible" reaction has been revealed, which is the disproportionation of the biradical back to the starting ketones. In addition, with increasing substitution α to the carbonyl function, α cleavage (the type I process) may be a competitive reaction.[4] Since the original discovery, the reaction has been extended to substances other than simple aldehydes and ketones.

In our general study of the photochemistry of the thione function we have found,[5] as have others,[6-8] several instances of behavior strikingly different from that of the carbonyl equivalent. This occurs most often when chemical reaction follows excitation to the S_2 state and it appears that many thiones, including those to be described, have lifetimes for the S_2 state of the order of 10^{-10} s.[5d,9,10] We were interested in two questions pertaining to the type II reaction as it applies to thiones. These were (a) whether molecules in the accessible $^3(n,\pi^*)$ state of the thione were energetically able to undergo the type II cleavage and whether orbital geometry was permissive,[11] and (b) whether, upon excitation into S_2, some other process might be observed. The geometrical requirements for interaction with this, most probably $^1(\pi,\pi^*)_1$ state could evidently be very different from those for the n,π^* state. The work to be described here answers these questions and provides the results of a kinetic investigation of the S_2 reaction.[12]

The only report in the literature pertinent to the present study was the account given by Barton and his co-workers[13] of the photolysis of certain thionoesters. These workers found that excitation of such compounds (as shown in A) led to a type II cleavage. For reaction to occur, activation of the relevant (γ) carbon-hydrogen bond was found to be necessary, typically by the proximity of unsaturation. Products derived from closure of the presumed 1,4-biradical were also isolated. Later work[14] established the intermediacy of the $^3(n,\pi^*)$ state and provided a mechanistic description of the overall process closely parallel to that of the type II. A preponderance of cleavage over cyclization or disproportionation processes was attributed to the greater energy of CO formation over olefin in the thionoester cleavage. In the absence of activation (bond dissociation energy (BDE) $\geqslant$380 kJ/mol) the cleavage was exceedingly slow and, at least in some cases, conversion to the S-esters was observed. An observation pertinent to the present study was that *the same photochemical consequences followed excitation into S_1 or S_2*: these states are separated by an energy gap of ca. 96 kJ/mol.



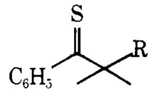
A

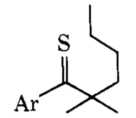
Results

Preparative. Previous preparations of aralkyl thiones[15,16] were of derivatives having a hydrogen atom α to the thiocarbonyl group. Such substances were not suitable for the present purposes, since they would be expected to undergo thioenolization.[17] To prohibit this and to discourage possible photochemical dimerization,[5g] a geminal dimethyl group was introduced. Solutions were degassed to exclude photooxidation.[18] The methods of preparation of the thiones were unexceptional and are described in the Experimental Section. The products lacking aromatic substitution all exhibited a long wavelength absorption band (λ_{max} 567 nm, $\epsilon \sim 110$) in cyclohexane, similar to that of thiobenzophenone.[19] This has been attributed to the $\pi^* \leftarrow$ n transition. A second band ($\pi^* \leftarrow \pi$) S_2($\lambda_{max} \sim$ 300 nm, $\epsilon \sim 4000$) was present, which shifted to longer wavelength from **1b** → **2** → **3**, which parallels the behavior in the equivalent thiobenzophenones and benzophenones. To higher energy there was a third band ($\lambda_{max} \sim 230$ nm, $\epsilon \sim 19\,000$) of undetermined nature which partially overlapped S_2. Excitation into S_2 or S_3 for compounds **1b, 1f, 1h, 2,** and **3,** led to fluorescence from S_2($\varphi_F \sim 0.005$), which has been discussed elsewhere.[9]

Preparative irradiations were conducted by irradiation with benzene as solvent through Pyrex with possible excitation in all bands and through a Corning 3-72 filter, which permitted excitation into S_1 specifically. Since reaction following the latter was exceedingly slow, the former may be regarded as leading essentially to reaction from the higher excited state.

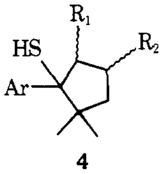
The behavior of **1a** was typical. Irradiation through Pyrex resulted in loss of the purple color and the formation of **4a**.





1a, R = $(CH_2)_2CH_3$
b, R = $(CH_2)_3CH_3$
c, R = $CH_2CH(CH_2)_2$
d, R = $(CH_2)_{10}CH_3$
e, R = $(CH_2)_3C_6H_5$
f, R = $CH_2CH(CH_3)(C_2H_5)$
h, R = CH_2CH_3
i, R = $(CH_2)_2C(CH_3)_3$

2, Ar = *p*-$MeOC_6H_4$–
3, Ar = *p*-$Me_2NC_6H_4$–



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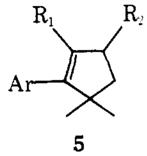

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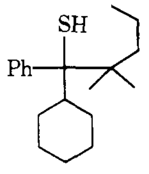
a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$
d, $R_1 = (CH_2)_7CH_3$; $R_2 = H$
e, $R_1 = C_6H_5$; $R_2 = H$
f, $R_1 = H$; $R_2 = CH_2CH_3$
g, $R_1 = CH_3$; $R_2 = CH_3$

Elemental analysis indicated an isomeric composition. Absorption at 2580 cm^{-1} and the presence of an exchangeable (D_2O) uncoupled proton at δ 1.84 in the ^{1}H NMR spectrum required the presence of a tertiary thiol. All five aromatic protons remained and the geminal dimethyl groups were now nonequivalent (δ 1.3, 0.63). Furthermore, the absence of the terminal methyl group suggested cyclization at that position. No molecular ion peak was observed in the mass spectrum, but

$M - H_2S$ and $M - (H_2S + CH_3)$ were evident, the latter being the base peak. Loss of H_2S could be induced chemically by reaction with phosphoryl chloride in pyridine or pyrolysis, but the most efficient process was treatment with mercuric acetate in acetic acid. With this reagent all cyclopentyl thiols mentioned in this paper were readily converted to the hydrocarbons. In many cases this facilitated purification, since the number of isomers was reduced. With the particular compound in question, the product (**5a**) was a previously reported substance and its physical properties agreed with those reported.[20] In addition, the olefinic proton (a triplet at δ 5.63) was shown to be coupled to the allylic methylene (δ 2.36), which was in turn, coupled with the methylene centered at δ 1.85. The geminal methyl groups appeared as a singlet. Of particular use in stereochemical assignment was the difference in chemical shift of the methyl groups in **4a:** that methyl group cis to the phenyl group appeared at higher field (δ 0.63) than did the trans (δ 1.03).[21]

The substances **4b–g** were similarly obtained as mixtures of isomers. Separation by GLC was not possible because of their instability and thin-layer chromatography was frequently inadequate; the hydrocarbons (**5b–g**) were obtained in pure form.

Irradiation of **1a** in cyclohexane, rather than the usual benzene, gave an additional compound (16%) whose composition was that of a 1:1 adduct of thione and solvent. A tertiary thiol was present (absorption at 2590 cm^{-1} and a singlet exchanged with D_2O at δ 1.30) and the structure **6** is probable both from the spectral data and by analogy with the behavior of adamantanethione. For the latter the nature of the thiol adduct has been established.[22] Photocycloaddition to the solvent occurred, as with other thiones, using acetonitrile. The product of this cycloaddition (**7**) has been reported elsewhere.[23]



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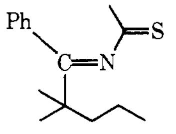

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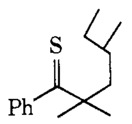

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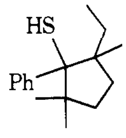
In none of the above reactions were products found arising from type I or type II photoprocesses. In particular, with **1d** no trace of undecene (β cleavage) nor C_{14} hydrocarbons (α cleavage) was detected by GLC.

Substances lacking α-hydrogen atoms (**1h, 1i**) reacted very slowly. After prolonged irradiation complex mixtures were obtained. These mixtures showed no high-field methyl signals nor exchangeable thiol protons. Because of the extended irradiation period, however, secondary reactions involving the thiol group cannot be excluded. With acetonitrile as solvent intermolecular reaction was possible and the related *N*-thioacetyl ketimines were isolated in high yield.[23]

Irradiation of **2** also led to the formation of the corresponding thiol, which could similarly be converted to the olefin. Irradiation of **2** at 366 nm also yielded the thiol. Irradiation of **3**, however, resulted in slow reaction and the formation of a complex mixture of products, which was not analyzed further.

The optically active thiones **1f** and **8** were prepared, having the chiral centers at the γ and δ positions, respectively. The first showed a positive Cotton effect in the 600-nm region ($[\alpha]_{564}$ 0°). The photoracemization was measured as follows. The disappearance of thione was measured optically and the rotation measured at the maximum of the ORD curve (602 nm).[24] The shape of this curve did not change even after 50% conversion, so it was assumed that the optical contribution of photoproducts in this region was negligible. Irradiation through Pyrex showed the same specific rotation after 42% conversion as before irradiation. Irradiation at long wavelength ($\lambda > 440$ nm) was much slower (2 mg/day) and after 34% conversion 28% racemization had occurred. Under the first conditions two thiols (**4f, 4g**) were obtained whose structures were established by conversion to the olefin. The products from long-wavelength irradiation were complex and insufficient amounts and difficulty of separation precluded the possibility of further study.

The thione **8** showed no Cotton effect, the dispersion curve being essentially plain, presumably because of the greater separation of the chiral center from the chromophore. A similar observation has been made with respect to aliphatic ketones.[25] Since the optical rotation was so small at long wavelength, the extent of photoracemization was followed by conversion of the remaining thione to the ketone (see Experimental Section). Irradiation of a benzene solution of **8** to 24% conversion (Pyrex) did not lead to detectable racemization. Isolation of the product gave a single thiol with three methyl singlets (δ 1.51, 1.13, and 1.04) and a further methyl (triplet) centered at δ 0.99. The thiol (exchanged with D_2O) appeared as a singlet at δ 1.54: it was, therefore, the expected thiol **9**.



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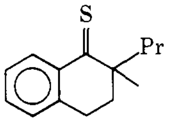

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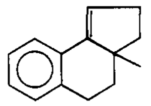

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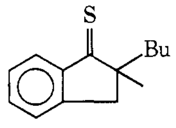

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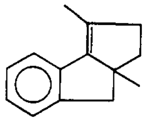


13

The photocyclization reaction was extended to the bicyclic thiones **10** and **12.** The thiols were not fully characterized, but were converted directly to the olefins **11** and **13.**

Mechanistic Studies. The variation in quantum yield of **4c** with respect to thione concentration was determined at 313 nm. Over the range 2×10^{-3}–3.8×10^{-2} M it remained constant both in the presence (0.034 ± 0.0007) and absence (0.035 ± 0.002) of oxygen. The quantum yield of disappearance of **1c** was also measured optically[26] and the values $(5.2 \pm 0.3) \times 10^{-2}$ (at 5.53×10^{-3} M) and $(5.3 \pm 0.3) \times 10^{-2}$ (at 1.52×10^{-4} M) were found.

The reaction at 313 nm could be quenched with biacetyl (Figure 1) and the extinction coefficient of this substance was sufficiently low at this wavelength for use at high concentration (with correction). However, in the presence of piperylene quenching appeared insignificant, the quantum yields of **4c** for 1.2, 1.7, and 2.3 M piperylene being 0.033, 0.031, and 0.034, respectively.

The quantum yield both in cyclohexane and, over a narrow range, benzene solution appeared to be wavelength independent within the S_2-S_3 bands (Table I). The quantum yield variation with solvent is contained in Table II. The reaction could not be induced by attempted sensitization with benzophenone (E_t = 288 kJ/mol), β-acetonaphthone (E_T = 248.3 kJ/mol), or chrysene (E_T = 240.4 kJ/mol).

The quantum yield of disappearance of **1c** was measured at 572 nm also. It was found to be at the limits of detection and $\leqslant 4.0 \times 10^{-5}$.

Discussion

The most immediately striking observation is that the products of excitation of the aralkyl thiones involve the δ C–H bond, i.e., are cyclopentane derivatives, and that these products

Table I. Variation of Quantum Yield of **4c** with Wavelength

	λ				
Solvent	250	288	298	313	334
Benzene			026	032	031
Cyclohexane	048	054		053	

Table II. Variation of Quantum Yield of **4c** with Solvent

Solvent	Quantum yield	Degassed
Acetonitrile	0.023	Yes
	0.025	No
Benzene	0.035	Yes
	0.035	No
Carbon tetrachloride	0.035	Yes
	0.033	No
Cyclohexane	0.049	Yes
	0.052	No
	0.053	Yes

are obtained following excitation into S_2 only. No cyclobutane, type II fission products, nor disproportionation products appear to accompany them. The reaction pathway is thus different from that of comparable ketonic systems.[3,4] The formation of cyclopentyl derivatives has been previously observed in the type II reaction, being favored both by activation of the δ position and for conformational reasons in particular compounds,[27] but the initial hydrogen-transfer step is the same whether cleavage, cyclobutane, or cyclopentane products are obtained. With the thiones the absence of δ hydrogen suppresses reaction even in the presence of γ hydrogen. This occurs whether the absence of the former be due to a short chain or because of substitution. A conformational preference for the δ position far higher than higherto observed would, if the pathway were similar, be required.

The reaction is quenched by biacetyl. This observation does not distinguish between the singlet (S_2) and a derived higher triplet (T_n): if the triplet energy of T_n be higher than that of S_1 the reactive state would not then be accessible from S_1. In contrast, the reaction is not quenched by over 2 M piperylene. We can conclude that biacetyl is quenching the singlet (S_2) and, assuming a diffusion-controlled energy transfer in hexane, we obtain a lifetime for S_2 of ~170 ps. The value obtained from fluorescence measurements already reported[9] is approximately 400 ps, which, considering the errors in both techniques, particularly in the quenching-rate assumption, is in fair agreement. That the reaction is suppressed by quenching of S_2 requires that the reactive state be derived from S_2, but does not require that it be S_2. If the reactive state were a higher triplet, the lack of quenching by 2 M piperylene could be merely an indication of a short lifetime. Assuming that quenching of about 10% could be detected, then the lifetime of the triplet would be of the order of 10^{-11}-5×10^{-12} s. The quantum yield of reaction is approximately 0.03, which requires that the rate constant for reaction be about 10^{10} s^{-1}. This seems an improbably high rate for a reaction involving the fission of a carbon–hydrogen bond which is not conformationally restrained. For comparison, hydrogen-abstraction rates in the type II process are one to three orders of magnitude less.[28]

The alternative is that the energy of the reactive triplet is above S_1 but below piperylene. This possibility appears excluded by the fact that we were unable to induce the reaction by triplet energy transfer from benzophenone, fluorenone, β-acetonaphthone, or chrysene. We are led, therefore, to believe that S_2 is the responsible state in the present group of substances.

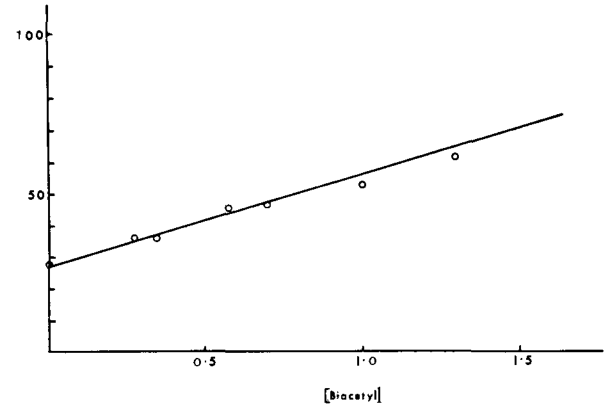


Figure 1. Plot of reciprocal quantum yield of cyclization against biacetyl concentration.

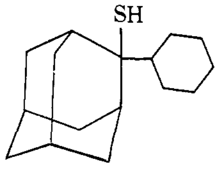
The S_2 state is most probably $\pi^* \leftarrow \pi$. The shift of the absorption maximum on substitution of the aromatic ring is analogous to that observed with thiobenzophenone and also with aryl ketones. As the S_1-S_2 separation decreases, a shorter lifetime for S_2 would be expected and is found.[9] With substance **2**, S_2 is still reactive, but the further decrease on going to **3** is such that internal conversion is fast enough to exclude reaction from the higher state. This situation is presumably that also obtaining in thionoesters.[14] The increasing CT contribution in the aryl thiones with substitution is compatible with the assignment.

With aromatic carbonyl compounds it is well established that hydrogen abstracting ability decreases with increasing π,π^* character.[29] In the present case a rate constant for reaction (assuming no reversibility) of $\sim 2 \times 10^8$ s^{-1} is obtained, which is high and may be an indication that hydrogen-atom abstraction is not the pathway chosen. As Salem and others have shown[30] the $^1(\pi,\pi^*)$ state correlates with a zwitterionic state of the products if hydrogen transfer be involved. With a different symmetry another reaction pathway is available: a concerted $2_\pi + 2_\sigma$ addition, a symmetry-allowed process in the excited state[31] wherein the exciting state does not correlate directly with the primary product, but with a singly excited state of it; the product is attained via an avoided crossing.[30] To attain this local symmetry the carbon–hydrogen bond must lie near the plane of the π bond and this, seemingly, may be achieved more easily in the δ, rather than the β or γ, position if the geometry of the excited thione is not too far removed from that of the ground state.[32] This process is compatible with, but not demanded by, the observed lack of racemization in recovered **8**. Lack of racemization has also been observed[3,4] in the decay of type II singlets and a singlet biradical pathway remains a possibility.

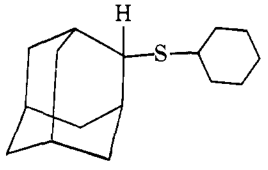
The reaction following excitation into S_1 was too slow to be studied in detail, since several days of irradiation were required for the conversion of very small amounts of thione. The quantum yield of the disappearance of **1c**, measured optically, was at the limits of detection ($\varphi < 4 \times 10^{-5}$) and a complex mixture was obtained. The recovery of racemized **1f** suggests that the excited molecule is, at least in part, following the ketonic pathway to the 1,4-biradical, followed by disproportionation to regenerate starting material; a process authenticated in detail with aralkyl ketones.[3]

The same substance, excited at short wavelength, reacted very much more rapidly, but the recovered starting material at partial conversion was unracemized. The possibility that the S_2 reaction involves prior interaction at the γ position, followed by efficient disproportionation and slower reaction at the δ position, thus appears excluded. The lack of racemization from the lower reactive state, arrived at by decay from the upper state, is merely a reflection of the very much faster reaction rate from S_2.

In the apparently equivalent intermolecular reaction of adamantanethione in the S_2 state with cyclohexane,[22] two products, **14** and **15,** are obtained. The present cyclization is the intramolecular equivalent of the formation of **14** and the intermolecular equivalent exists in **6**. As yet we have not observed the formation of the equivalent of **15**, i.e., **16**, although



14



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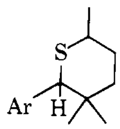
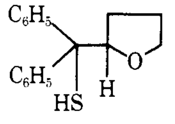


16

there is no obvious stereochemical impediment. In the case of thiobenzophenone, such products (**17** and **18**) have been observed as the result of an intermolecular process, but here the excited state(s) responsible for reaction is uncertain.[33] The situation may be complicated both inter-[33] and intramolecularly[12] by the presence of a heteroatom when electron-transfer processes leading to biradicals become, in principle, possible.[34a,b]



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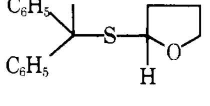

18

Experimental Section

General Procedures. NMR spectra were obtained in carbon tetrachloride solution unless otherwise stated and are given in parts per million from internal Me_4Si. Mass spectra were obtained on an M-66 at 70 eV, relative intensities being given parenthetically. Optical rotation data were obtained with a JASCO ORD/UV-S/CD-1 spectrometer. Melting and boiling points are uncorrected; temperatures recorded for bulb-to-bulb distillation are external; petroleum ether (PE) refers to the fraction of boiling range 60–80 °C; silica gel for thin-layer chromatography (TLC) was GF-254 (Merck). For vapor-phase chromatogrphy (VPC) the following columns were used with an Aerograph 1700 (thermal conductivity detector): (A) 15% FFAP on Chromosorb W, 80/100 (HP), ¼ in. × 6 ft; (B) 10% SE 30 on Chromosorb W, 80/100 (acid washed), ¼ in. × 6 ft; (C) 10% Carbowax 20 M on Chromosorb P, 80/100 (acid washed), ¼ in. × 6 ft.

Preparative Photochemistry. Reactions were carried out near room temperature using a 450-W Hanovia medium-pressure lamp in a quartz immersion well. A Pyrex filter was used for short-wavelength irradiations and a Corning 3-72 cut-off filter for long-wavelength irradiations, unless otherwise noted. Solutions were degassed (freeze-pump-thaw) to a residual pressure of $2\text{–}5 \times 10^{-5}$ Torr. Percentage conversions were measured optically.

Ketone Preparations. The following were prepared as previously described: α,α-dimethylvalerophenone[35] (**1a**; S = O), α,α-dimethylhexanophenone[36] (**1b**; S = O), α,α,γ-trimethylvalerophenone[37] (**1c**; S = O), α,α-dimethyl-δ-phenylhexanophene[38] (**1e**; S = O), α,α-dimethyltridecanophenone[39] (**1d**; S = O), and α,α-dimethylbutyrophenone[40] (**1h**; S = O).

(4*S*)-1-Phenyl-2,2,4-trimethyl-1-hexanone (1f; S = O). A stirred mixture of isobutyrophenone (8.8 g) and sodium amide (2.4 g) in dry toluene (150 ml) was refluxed for 3 h (N_2). The reaction mixture was heated to 70 °C and (*S*)-(+)-1-bromo-2-methylbutane[41] (10.7 g) in toluene (50 ml) was added dropwise. After stirring at 90 °C for 22 h, the reaction was quenched with acidic ice-water (acetic acid). Fractional distillation of the isolated product gave 7 g (53%) of the ketone (**1c**; S = O): bp 106–107 °C (2 mm); $[\alpha]^{20}\text{D}$ 12.7 °C (c 6.3, dioxane); $\nu_{\max}$ (film) 1670, 1595, 1575, 720, and 700 cm^{-1}; ^{1}H NMR δ 7.62 and 7.30 (m, 5, arom), 1.26 (s, CMe_2); mass spectrum m/e 218 (M^+, 2) 148 (43), and 105 (100). Anal. Calcd for $C_{15}H_{22}O$: m/e 218.1669. Found: 218.1672.

(5*S*)-1-Phenyl-2,2,5-trimethyl-1-heptanone (8; S = O). (*S*)-3-methyl-1-pentanol was prepared as follows. To the mechanically stirred Grignard reagent solution from (*S*)-(+)-1-bromo-2-methylbutane (74 g) and magnesium turnings (12.1 g) in ether (600 ml), formaldehyde[43] was slowly added (N_2). After standing at room temperature for 6 h, the reaction was cautiously poured into ice-ammonium sulfate. Fractional distillation of the isolated product afforded the alcohol, 34 g (68%): bp 67–68 °C (18 mm); $[\alpha]^{18}\text{D}$ 8.23° (neat) [lit.[44] bp 154 °C, $[\alpha]^{17}\text{D}$ 8.2°]. The corresponding bromo derivative was prepared by treatment of the alcohol with 48% hydrobromic acid and sulfuric acid. Extraction of the unreacted alcohol and distillation gave (*S*)-(+)-1-bromo-3-methylpentane in 66% yield: bp 144–145 °C; $[\alpha]^{18}\text{D}$ 18.9° (neat) [lit.[45] bp 146–146.8 °C, $[\alpha]^{19}\text{D}$ 19.97°]. Condensation of isobutyrophenone enolate anion (from 29.6 g of ketone and 8 g of sodium amide in 500 ml of toluene) with the above bromo derivative and following the same procedure as that for **4f** gave **8**; S = O (28 g, 61%): bp 114.5–115.5 °C (1 mm); $[\alpha]^{18}\text{D}$ 6.0° (c 27.5 in isooctane); $\nu_{\max}$ (CCl_4) 1670, 1600, 1580, and 695 cm^{-1}; ^{1}H NMR δ 7.62 and 7.30 (m, 5, arom); 1.26 (s, CMe_2), and 0.86 (br t); mass spectrum m/e 232 (M^+, 2), 148 (69), and 105 (100). Anal. Calcd for $C_{16}H_{24}O$: m/e 232.1825. Found: 232.1837.

1-Phenyl-2,2,5,5-tetramethyl-1-hexanone (1i; S = O). To a stirred solution of the Grignard reagent (from 1-bromo-4,4-dimethylpentane[46] (78 g) and magnesium turnings (9.9 g) in anhydrous ethyl ether (500 ml)), benzonitrile (41.2 g) was added. After refluxing for 5 h, the reaction mixture was acidified (2.5% hydrochloric acid). The aqueous layer was refluxed for 15 min and extracted with ethyl ether. The ethereal layer was dried ($MgSO_4$), concentrated, and distilled to give the ketone, 49.7 g (61%): bp 135–136 °C (7 mm) [lit.[47] bp 141 °C (8 mm)]. A mixture of this ketone (34 g) and sodium amide (14 g) in ether (400 ml) was stirred at room temperature for 3 h and methyl iodide (70 g) was added. After 12 h of reflux the reaction mixture was poured into water, the ethereal solution washed with tartaric acid (0.05 M), sodium thiosulfate (0.05 M), $NaHCO_3$ solution, and water. It was then concentrated and distilled to give 32 g of the ketone **4i** (82%): bp 137 °C (7 mm); $\nu_{\max}$ (neat) 1675, 1600, 1580, 710, and 695 cm^{-1}; ^{1}H NMR δ 7.8 and 7.5 (m, 5, arom), 1.72 (m, 2) and 1.08 (m, 2) (AA′BB′, CH_2CH_2), 1.27 (s, 6, CMe_2), and 0.80 (s, 9, CMe_3); mass spectrum m/e 232 (M^+, 1), 148 (30), and 105 (100). Anal. Calcd for $C_{16}H_{24}O$: m/e 232.1821. Found: 232.1820.

1-*p*-Anisyl-2,2-dimethyl-1-hexanone (2; S = O). This was prepared by condensation of *p*-methoxyisobutyrophenone[48] enolate anion (from 20 g of ketone and 5.3 g of sodium amide in 270 ml of toluene) with 1-bromobutane in 57% yield (16.5 g): bp 99–102 °C (0.05 mm); $\nu_{\max}$ (film) 1665, 1600, 1575, 1255, and 840 cm^{-1}; mass spectrum m/e 234 (M^+, 2), 178 (6), and 151 (100). Anal. Calcd for $C_{15}H_{22}O_2$: m/e 234.1618. Found: 234.1625.

1-*p*-Dimethylaminophenyl-2,2-dimethyl-1-hexanone (3; S = O). This was prepared using *p*-dimethylaminoisobutyrophenone enolate anion[49] (from 12.7 g of ketone and 3.1 g of sodium amide in 150 ml of toluene). The product was obtained in 59% yield (9.8 g) after one crystallization and the crude ketone (mp 61–64 °C) was used without further purification.

2-Methyl-1-tetralone. Ethyl 1-keto-1,2,3,4-tetrahydro-2-naphthoate[50] (5.55 g) was added to a solution of sodium (0.68 g) in absolute alcohol (50 ml) and methyl iodide (6.4 g) was added, the mixture being refluxed for 20 h. Decomposition with water and isolation with methylene chloride gave material which, after solvent removal, was refluxed with a mixture of acetic acid (40 ml), sulfuric acid (5 ml), and water (25 ml) for 21 h. Isolation of the product and distillation gave the tetralone (3.7 g, 82%): bp 139–140 °C (16 mm) (lit.[51] 136–138 °C (16 mm)).

2-Methyl-2-propyl-1-tetralone. A solution of methyl tetralone (7.9 g, 0.05 M) in dry toluene (100 ml) was refluxed with sodium amide (2.4 g) for 3 h with stirring. Propyl iodide (8.5 g) was added at room temperature and the mixture refluxed overnight. Decomposition with ice water and isolation of the product in the usual way followed by distillation (bp 106–110 °C (0.4 mm)) gave the tetralone (8.6 g), which was converted into the thione without further purification.

2-Methyl-2-butyl-1-indanone. 2-Methyl-1-indanone was prepared by the procedure of Burckhalter and Fuson.[52] This was alkylated by the procedure described for the indanone, the crude ketone being obtained in 85% yield (bp 128–131 °C (14 mm)).

Preparation of Thiones. All thiones (except **2** and **3**) were prepared from the corresponding ketone by one of the procedures indicated below.

Procedure A. Dry HCl and H_2S were bubbled through a solution (−10 °C) of ketone (10–15 mmol) in absolute ethanol for 6–7 h. The mixture was poured into water, isolated with PE, washed, and chromatographed over silica gel (~100 g). The purple band was bulb-to-bulb distilled, rechromatographed, and redistilled when, in most cases, a product of >98% purity was obtained.

Procedure B.[53] Hydrogen sulfide (~5 ml) was condensed (−78 °C) into a solution of ketone (10 mmol) in absolute ethanol. Dry HCl was passed until the purple color reached its maximum intensity (0.5–3 h), when the mixture was poured into water–PE. Purification was as under procedure A. Thiones were stored in vacuum-sealed tubes and purified again prior to use.

1-Phenyl-2,2-dimethyl-1-pentanethione (1a). Procedure A (45–65%), bulb-to-bulb distillation at 58–60 °C (0.1 mm): $\lambda_{max}^{C_6H_{12}}$ 567, 298, and 230 nm (ϵ 110, 3900, and 9700); NMR δ 1.33 (s, 6 H); mass specturm *m/e* 206 (M^+, 16), 164 (28), and 121 (100). Anal. Calcd for $C_{13}H_{18}S$: *m/e* 206.1125. Found: 206.1125.

1-Phenyl-2,2-dimethyl-1-hexanethione (1b). Procedure A (55–70%), bulb-to-bulb distillation at 60–64 °C (0.4 mm): mass spectrum *m/e* 220 (M^+, 14), 164 (32), and 121 (100). Anal. Calcd for $C_{14}H_{20}S$: *m/e* 220.1285. Found: 220.1287.

1-Phenyl-2,2,4-trimethyl-1-pentanethione (1c). Procedure B (58%), bulb distillation at 60–65 °C (0.5 mm): mass spectrum *m/e* 220 (M^+, 1), 164 (70), and 121 (100). Anal. Calcd for $C_{14}H_{20}S$: *m/e* 220.1285. Found: 220.1300.

1-Phenyl-2,2-dimethyl-1-tridecanethione (1d). Procedure A (35%), reaction temperature 0 °C, bulb distillation at 140–145 °C (0.09 mm): mass specturm *m/e* 318 (M^+, 12), 164 (98), and 121 (100). Anal. Calcd for $C_{21}H_{34}S$: *m/e* 318.2380. Found: 318.2351.

1,5-Diphenyl-2,2-dimethyl-1-pentanethione (1e). Procedure B (39%), bulb distillation 120–130 °C (0.1 mm): mass spectrum *m/e* 282 (M^+, 13), 164 (13), and 121 (100); $\delta_{max}^{C_6H_{12}}$ 67, 295, and 228 nm (ϵ 109, 4100, and 9900). Anal. Calcd for $C_{19}H_{22}S$: *m/e* 282.1441. Found: 282.1449.

(4*S*)-1-Phenyl-2,2,4-trimethyl-1-hexanethione (1f). Procedure B (62%), bulb distillation at 70–77 °C (0.2 mm): $[\alpha]^{22}$650 69°, $[\alpha]^{22}$600 174°, $[\alpha]^{22}$564 0°, $[\alpha]^{22}$510 −159°, $[\alpha]^{22}$425 −97°, and $[\alpha]^{22}$350 −205° (*c* 0.49, benzene); mass spectrum *m/e* 234 (M^+, 2), 164 (75), and 121 (100). Anal. Calcd for $C_{15}H_{22}S$: *m/e* 234.1441. Found: 234.1461.

1-Phenyl-2,2-dimethyl-1-butanethione (1h). Procedure A (62%), bulb distillation at 62–66 °C (0.8 mm): $\lambda_{max}^{C_6H_{12}}$ 567, 297, and 228 nm (ϵ 110, 4000, and 10 400); mass spectrum *m/e* 192 (M^+, 30) and 121 (100). Anal. Calcd for $C_{12}H_{16}S$: *m/e* 192.0969. Found: 192.0977.

1-Phenyl-2,2,5,5-tetramethyl-1-hexanethione (1i). Procedure B (56%), bulb distillation at 72–75 °C (0.1 mm): NMR δ 1.30 (s, 6 H, CMe_2) and 0.81 (s, 9 H, CMe_3); mass spectrum *m/e* 248 (M^+, 20), 164 (27), and 121 (100). Anal. Calcd for $C_{16}H_{24}S$: C, 77.37; H, 9.74; S, 12.88. Found: C, 77.14; H, 9.49; S, 12.73.

(5*S*)-1-Phenyl-2,2,5-trimethyl-1-heptanethione (8). Procedure B (53%), bulb distillation at 75–82 °C (0.1 mm): $[\alpha]^{22}$680 2°, $[\alpha]^{22}$680 0°, $[\alpha]^{22}$450 20°, and $[\alpha]^{22}$400 23° (*c*, 0.22, benzene); mass spectrum *m/e* 248 (M^+, 14), 164 (38), and 121 (100). Anal. Calcd for $C_{16}H_{24}S$: *m/e* 248.1598. Found: 248.1617.

1-*p*-Anisyl-2,2-dimethyl-1-hexanethione (2). Procedure B (45%), complete separation required preparative TLC (PE–CH_2Cl_2, 7:15). Bulb distillation at 102–105 °C (0.05 mm): $\nu_{max}^{C_6H_{12}}$ 568, 334, 236, and 225 nm (ϵ 210, 9200, 10 800, and 11 200); ν_{max} (film) 1600, 1575, 1250, and 830 cm^{-1}; mass spectrum *m/e* 250 (M^+, 5), 194 (15), and 151 (100). Anal. Calcd for $C_{15}H_{22}O_5$: *m/e* 250.1390. Found: 250.1398.

1-*p*-Dimethylaminophenyl-2,2-dimethyl-1-hexanethione (3). This was prepared by the method of Scheeren et al.[54] To a stirred solution of **14** (2.5 g) and P_4S_{10} (6.7 g) in acetonitrile (25 ml) was added $NaHCO_3$ (5 g) in small portions. After stirring for 12 h at 30 °C the mixture was diluted with ether, washed (5% aqueous $NaHCO_3$), and the product after evaporation of the solvent chromatographed over silica gel (PE–ethyl acetate, 95:5). Further purification (TLC, PE–ethyl acetate, 95:7) gave the thione (0.58 g, 22%) as a brown oil, bulb distillation at 105–115 °C (0.05 mm): mp ~15 °C; $\lambda_{max}^{C_6H_{12}}$ 570, 395, 322, 310, and 257 nm (ϵ 550, 18 000, 1200, 1100, and 10 500); λ_{max}^{MeCN} 557, 420, 325, 313, and 257 nm (945, 18 100, 1100, 1100, and 10 300); mass spectrum *m/e* 263 (M^+, 12), 207 (16), and 164 (100). Anal. Calcd for $C_{16}H_{25}NS$: *m/e* 263.1707. Found: 263.1707.

2-Methyl-2-Propyl-1-thiotetralone (10). The crude ketone (2 g) was refluxed for 8 h in dry pyridine (120 ml) containing P_2S_5 (10 g) using the procedure of Greidanus.[55] Dilution with PE, filtration, and evaporation of the solvent gave an oil which was chromatographed over silica gel (eluent, benzene–PE, 1:9) and finally purified by TLC and distillation to give the thione **10** (920 mg, 48%) $\nu_{max}^{CCl_4}$ 1250, 1160, 1100, 1060, 870, and 695 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 230, 235 (inf), 250 (inf), 315, and 588 nm (ϵ 8120, 7375, 2680, 12 100, and 44); mass spectrum *m/e* 218 (M^+, 9), 176 (100), 161 (14), 160 (16), 148 (14), 143 (28), 134 (14), 128 (14), and 115 (15). Anal. Calcd for $C_{14}H_{18}S$: *m/e* 218.1129. Found: 218.1120.

2-Methyl-2-butyl-1-thioindanone (12). This was prepared from the ketone in 51% yield following the procedure for the tetralone: $\nu_{max}^{CCl_4}$ 1600, 1580, 1280, 1250, 1150, 1060, 870, 780, and 695 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 296 (inf), 309, 324, 548, and 587 nm (ϵ 11 100, 13 600, 13 800, 18, and 17); mass spectrum *m/e* 218 (M^+, 7), 175 (13), 162 (100), and 142 (12). Anal. Calcd for $C_{14}H_{18}S$: *m/e* 218.1129. Found: 218.1121.

Irradiation of 1a in Benzene. The thione (150 mg) in benzene (25 ml) was irradiated to 95% conversion (20 h). Preparative TLC (PE) gave **4a** (105 mg; 70%), distilled at 70–74 °C (0.2 mm): ν_{max} (film) 2580 and 695 cm^{-1}; NMR δ 1.84 (s, 1 H, exchanged with D_2O, SH), 1.3, and 0.63 (s, 3 H each CMe_2 trans and cis to phenyl); mass spectrum *m/e* 172 ($M^+ - H_2S$, 42) and 157 (100). Anal. Calcd for $C_{13}H_{18}S$: C, 75.69; H, 8.80; S, 15.51. Found: C, 75.48; H, 8.68; S, 15.45.

To a stirred solution of **4a** (100 mg) in glacial acetic acid (2 ml), mercuric acetate (175 mg) was added in one portion. The yellow color changed to a black precipitate and finally to a white precipitate. After 30 min the mixture was diluted with chloroform and filtered through Celite. The clear solution was washed (aqueous $NaHCO_3$) and the product isolated by preparative TLC (PE) to give **5a**[56] (83 mg; 93%): $\nu_{max}^{CCl_4}$ 1600, 1500, and 700 cm^{-1}; mass spectrum *m/e* 172 (M^+, 52) and 157 (100).

Irradiation of 1a in Cyclohexane. The thione (110 mg) in cyclohexane (30 ml) was irradiated through Pyrex to complete conversion (16 h). Preparative TLC (PE) gave two products. The slower moving (66 mg, 60%) was the thiol **4a.** The faster moving (17 mg, 16% after distillation at 110–115 °C (0.1 mm)) was the thiol **6**: $\nu_{max}^{CCl_4}$ 2590 and 695 cm^{-1}; NMR δ 1.3 (s, 1 H, exchanged with D_2O), 0.96, and 0.93 (s, 3 H each, CMe_2); mass spectrum *m/e* 256 ($M - H_2S$, 2), 121 (60), 119 (100), and 117 (96). Anal. Calcd for $C_{19}H_{30}S$: C, 78.57; H, 10.41; S, 11.02. Found: C, 78.69; H, 10.23; S, 10.97.

Irradiation of 1b. The thione (100 mg) was irradiated in a similar manner in benzene to give the stereoisomeric thiols (75 mg, 75%). Anal. Calcd for $C_{14}H_{20}S$: C, 76.32; H, 9.15; S, 14.53. Found: C, 76.70; H, 8.88; S, 14.55.

Treatment of the thiols (30 mg) with mercuric acetate gave the olefin **5b** (22 mg; 87%), distilled at 42–45 °C (0.1 mm): $\nu_{max}^{CCl_4}$ 1600, 1570, and 700 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 235 nm (ϵ 4600); NMR δ 2.32 (2 H, allylic CH_2), 1.50 (near s, 3 H, vinyl methyl), and 1.02 (s, 6 H, CMe_2); mass spectrum *m/e* 186 (M^+, 23) and 171 (100). Anal. Calcd for $C_{14}H_{18}$: *m/e* 186.1404. Found: 186.1410.

Irradiation of 1c. The thione (120 mg) gave 107 mg of thiol (**4c**) (90%), which distilled at 68–78 °C (0.3 mm): ν_{max} (film) 2580 and 695 cm^{-1}; NMR δ 1.66 (s, 1 H, exchanged with D_2O), 1.3 (s, 3 H, Me trans to phenyl), 1.13 (d, 6 H, J = 6 Hz), and 0.63 (s, 3 H Me cis to phenyl); mass spectrum *m/e* 186 ($M - H_2S$, 54) and 171 (100). Anal. Calcd for $C_{14}H_{20}S$: C, 76.32; H, 9.15; S, 14.53. Found: C, 75.51; H, 9.15; S, 14.39.

Conversion of the thiol **4c** (45 mg) to the olefin **5c** was accomplished in 89% yield: $\nu_{max}^{CCl_4}$ 1600 and 695 cm^{-1}; mass spectrum *m/e* 186 (55) and 171 (100). Anal. Calcd for $C_{14}H_{18}$: *m/e* 186.1404. Found: 186.1407.

Irradiation of 1c above 445 nm. The thione (20 mg) in benzene (5 ml) was irradiated to complete conversion (two 450-W lamps, Corning 3-72 filter, 12 days). Thin-layer chromatography showed a minimum of nine products. No peak corresponding to **4c** was found on VPC (column A, 170 °C).

Similar experiments with **1a** and **1b** also did not yield detectable amounts of cyclopentyl derivatives.

Irradiation of 1d. The thione (79 mg) in benzene (10 ml) gave 58 mg (69%) of **4d** (distilled 135–140 °C (0.2 mm)): $\nu_{max}^{CCl_4}$ 2590 and 695 cm^{-1}; mass spectrum *m/e* 284 ($M - H_2S$, 16) and 269 (100). Anal. Calcd for $C_{21}H_{34}S$: C, 79.19; H, 10.76; S, 10.05. Found: C, 79.27; H, 10.66; S, 10.15. The thiol (75 mg) was converted to the olefin

(63 mg, 94%) as before and distilled (84-89 °C (0.2 mm)): $\nu_{max}^{CCl_4}$ 1600 and 695 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 235 nm (ϵ 5000); NMR δ 2.33 (m, 2 H, allylic) and 0.96 (s, 6 H, CMe$_2$); mass spectrum *m/e* 284 (M$^+$, 15) and 269 (100). Anal. Calcd for $C_{21}H_{32}$: *m/e* 284.2502. Found: 284.2491.

The thione (79 mg) in benzene was irradiated through Pyrex to complete conversion (9 h). The product mixture was analyzed by direct injection of 10 μl (column B, 105 °C), but no peak corresponding to 1-undecene (5 min) was observed. The limits of detection were such to require <2% cleavage. No peaks corresponding to the hydrocarbons from α cleavage were observed (column B, 125 °C). Irradiation of the corresponding ketone showed a large peak corresponding to 1-undecene and two smaller (2.8 and 3.4 min), perhaps derived from α cleavage.

Irradiation of 1e. The thione (155 mg) in benzene (10 ml) was irradiated through Pyrex (11 h) and separation of the product by preparative TLC (PE-benzene, 9:1) gave the thiols (**4e**) (97 mg, 70%); mass spectrum *m/e* 248 (M − H$_2$S, 60) and 233 (100). Anal. Calcd for $C_{19}H_{22}S$: C, 80.81; H, 7.85; S, 11.33. Found: C, 80.90; H, 7.96; S, 11.43.

The thiols (**4e**) (120 mg) were converted to hydrocarbon (**5e**) (91 mg, 86%) as before: mp 59-62 °C; $\nu_{max}^{CCl_4}$ 1600 and 695 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 259 nm (ϵ 13 200); mass spectrum *m/e* 248 (M$^+$, 60) and 233 (100). Anal. Calcd for $C_{19}H_{20}$: *m/e* 248.1564. Found: 248.1549.

Irradiation of 1f. The thione (113 mg) in benzene was irradiated (9 h; 95% conversion) and the product separated by preparative TLC (PE) to give the thiols **4g** (faster band, 57 mg, 53%) and **4f** (36 mg, 31%).

The thiol **4g** (distilled at 65-70 °C (0.1 mm)): $[\alpha]^{22}\mathrm{D}$ −37° (*c* 1.4, benzene); NMR δ 1.35 (s, 1 H, exchanged D$_2$O), 1.21 (s, 3 H, CMe trans to phenyl), and 0.55 (s, 3 H, CMe cis to phenyl); mass spectrum *m/e* 200 (M − H$_2$S, 28) and 185 (100). Anal. Calcd for $C_{15}H_{22}S$: C, 76.88; H, 9.46; S, 13.66. Found: C, 76.99; H, 9.59; S, 13.59.

The thiol **4g** (109 mg) was converted to the olefin **5g** (80 mg, 85%) (distilled at 48-52 °C (0.1 mm)): $\nu_{max}^{CCl_4}$ 1600 and 695 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 235 nm (ϵ 4500); NMR δ 1.1 (d, 3 H, CHMe), 1.02, and 1.00 (s, 3 H each); mass spectrum *m/e* 200 (M$^+$, 23) and 185 (100). Anal. Calcd for $C_{15}H_{20}$: *m/e* 200.1564. Found: 200.1563.

The thiol **4f** could not be obtained free of thiol **4g** and so was converted to the olefin (90%), when **5f** and **5g** were obtained in a ratio of about 4:1. Preparative TLC (silicic acid-9% AgNO$_3$; PE-CH$_2$Cl$_2$, 19:1) permitted the isolation of **5f** (slower band; distilled at 50-52 °C (0.1 mm): $\nu_{max}^{CCl_4}$ 1600, 1570, and 695 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$ 247 nm (ϵ 9500); NMR δ 5.59 (d, 1 H, J = 2 Hz), 1.21, 1.16 (s, 3 H each), and 0.94 (quasi t, $J \approx 7$ Hz, CH$_2$CH$_3$); mass spectrum *m/e* 200 (M$^+$, 18), 185 (9), and 171 (100). Anal. Calcd for $C_{15}H_{20}$: *m/e* 200.1564. Found: 200.1567.

Irradiation of 2. A solution of the thione (109 mg) in benzene was irradiated at 366 nm (Corning 0-52 and 7-60 filters) to complete conversion (~100 h). Preparative TLC (PE-CH$_2$Cl$_2$, 1:1) afforded one major product (**4b**; Ar = *p*-MeOC$_6$H$_4$-) (71 mg, 65%), distilled at 82-90 °C (0.07 mm): $\nu_{max}^{CCl_4}$ 2580, 1610, 1250, and 830 cm^{-1}; mass spectrum *m/e* 216 (M − H$_2$S, 34) and 201 (100). This was converted (77 mg) to the olefin (**5b**; Ar = *p*-MeOC$_6$H$_4$-) (55 mg, 83%), distilled at 78-84 °C (0.06 mm): $\nu_{max}^{CCl_4}$ 1600, 1665, 1500, 1240, and 830 cm^{-1}; NMR δ 3.74 (s, 3 H, OMe), 1.49 (near s, 3 H, C(CH$_3$) = 6), and 1.00 (s, 6 H); mass spectrum *m/e* 216 (M$^+$, 36) and 201 (100). Anal. Calcd for $C_{15}H_{20}O$: *m/e* 216.1513. Found: 216.1523.

Similar irradiation of **3** (λ > 300 or >520 nm) was very slow and gave a complex mixture which was not further investigated.

Irradiation of 1i. The thione (20 mg) in benzene (5 ml) was irradiated (60% conversion) for 100 h in a Rayonet reactor with RUL 300-nm lamps. Under similar conditions the complete conversion of **1a** requires <10% of this time. A complex mixture was obtained from which, in the NMR spectrum, high-field signals were absent: exchangeable SH signals were also not detectable. Under the same conditions the reaction of **1h** was even slower.

Photoracemization of 8. A solution of the thione (470 mg) in benzene (50 ml) was divided into two portions which were degassed separately. One was irradiated for 8 h (24% conversion). The contents of each tube was treated with mercuric acetate (440 mg) in acetic acid-chloroform (3:1) for 30 min, water added, the product isolated, and the corresponding ketone isolated by preparative TLC (PE-CH$_2$Cl$_2$, 9:16) and distilled (70% yield). The rotations obtained (5-cm path) are as follows (wavelength, reference, irradiated material): 600 nm, 5.4 ± 0.2 and 5.3 ± 0.2; 500 nm, 7.8 ± 0.2 and 7.6 ± 0.2; 400 nm, 11.6 ± 0.2 and 11.5 ± 0.2.

Photoracemization of 1f. (a) λ > 445 nm. A 2.2×10^{-2} M solution of the thione in benzene was degassed. The initial rotation was $[\alpha]^{22}602$ 171°. After irradiation (4 days, 28% conversion) the rotation was $[\alpha]^{22}602$ 113° (34% racemization). (b) λ > 280 nm. A solution of thione (30.2 mg) in benzene (5 ml), $[\alpha]^{22}602$ 172°, was irradiated through Pyrex to 42% conversion (35 min). The rotation was $[\alpha]^{22}602$ 168°.

Irradiation of the Thiotetralone (10). A solution (5×10^{-3} M, 150 ml) in benzene was irradiated for 24 h. TLC (benzene-PE, 1:9) afforded the crude thiol. To the thiol from the irradiation of 500 mg of thione in glacial acetic acid (10 ml) was added mercuric acetate (800 mg) and the mixture was stirred 2 h. After filtration through Celite the product was isolated with chloroform and purified by TLC (PE) to give the olefin **11** (306 mg, 72%): $\lambda_{max}^{C_6H_{12}}$ 258 nm (ϵ 7560); mass spectrum *m/e* 184 (M$^+$, 50), 169 (100), 141 (31), 128 (21), and 115 (15). Anal. Calcd for $C_{14}H_{16}$: *m/e* 184.1251. Found: 184.1245.

Irradiation of the Thioindanone 12. A solution of the thione (5×10^{-3} M, 150 ml) was irradiated in benzene (24 h). The thiol (from 300 mg thione) was treated with mercuric acetate in acetic acid as described above to give the hydrocarbon **13** (172 mg, 69%): $\lambda_{max}^{C_6H_{12}}$ 259 nm (ϵ 7900); mass spectrum *m/e* 184 (M$^+$, 38), 169 (100), 154 (15), 141 (15), 128 (17), 119 (37), and 117 (38). Anal. Calcd for $C_{14}H_{18}$: *m/e* 184.1251. Found: 184.1259.

Kinetic Studies. Acetonitrile was refluxed over phosphorus pentoxide for 10 h and fractionally distilled. Piperylene was fractionated just before use. Analysis of **1c** was by VPC on a 6 ft glass column, 15% FFAP on Chromosorb P at 135 °C (injector, 120 °C) using a flame detector. The calibration compound was dibenzofuran. The exciting light was an Osram HBO 200-W high-pressure mercury arc using chemical filters[57] and a 0.25-m Jobien-Yvon monochrometer or (286 nm) an interference filter. Ferrioxalate actinometry was used.[58]

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Electronic Excited States of Small Ring Compounds 3: Cyclopropene, Vinylcarbene, and Vinylmethylene[1]

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Abstract: The 3,3-isopyrazoles IIa–e have been prepared. Irradiation of IIa–e produces the vinyl diazo compounds IXa–e. When the vinyl diazo compounds IXa–e are irradiated at 10 °C the cyclopropenes Xa–d result in high yields. When the irradiation of the vinyl diazo compounds IXa–d is carried out at ca. 5 K in rigid medium (MCIP), the ESR spectrum indicates a stable triplet species is produced. The vinylmethylene structure Ia–d has been assigned to these triplet species. The temperature dependence (5–30 K) of the ESR signal due to Ia–d indicates the triplet is the ground state and that the singlet is not thermally populated within this temperature range. In contrast, no triplet signal was detected upon irradiation of IIe under these conditions and it is proposed that Ie is a ground-state singlet species. The involvement of vinylcarbene and/or vinylmethylene as intermediates in the preparation and photochemical reaction of cyclopropenes is discussed. Some limitations of the temperature-dependent ESR signal intensity approach for the determination of the energy separation of equilibrating singlet and triplet states are pointed out.

Introduction

We have a continuing interest in the mechanism(s) for the interconversion and the relative energies of three-membered rings and the corresponding heterolytic and homolytic bond-cleaved species.[4] Vinylmethylene and/or vinylcarbene have frequently been proposed as intermediates in the preparation and photochemical and thermal reactions of cyclopropenes. However, direct evidence of their involvement, insight into the structure and nature of these species, and even knowledge as to which is the ground state was not available at the onset of this work. In this regard, the theoreticians were several years ahead of the experimentalists; at least two groups have discussed the problem in some detail.[5]

In this paper, we will report the details of our preliminary account of the preparation and characterization of the vinylmethylenes Ia and Id and vinylcarbene Ie.[6] In addition we have prepared the 4-methoxy (Ib) and 4-cyano (Ic) derivatives and can now report the effect of these electron-donating and electron-withdrawing substituents on the vinylmethylene. Since

Arnold et al. / Excited States of Small Ring Compounds