nance of hydrocarbon even in the presence of excess triphenylphosphine suggests the failure of the benzyl group in **2** (R = $PhCH_2$–) to undergo the migratory insertion required for the formation of the acyl iron anion **4** (R = $PhCH_2$–). Apparently, the more stable benzyl–iron bond favors the alkyl form **2**.[10]

Conversion of 1-bromononane to decanal illustrates a typical procedure. A dry reaction vessel was flushed with N_2, followed by the addition of 2 ml of 1% sodium amalgam[11] and 12 ml of dry THF. With vigorous magnetic stirring under N_2 there was added 185 μl (1.38 mmol) of commercial iron pentacarbonyl,[12] causing immediate evolution of CO and partial separation of the colorless salt **1**. The mixture was stirred for 1 hr at 25° and the amalgam was removed through a side arm. A solution of 320 mg (1.2 mmol) of triphenylphosphine in 2 ml of dry THF was added, followed by the addition of 188 μl (1.0 mmol) of 1-bromononane. The mixture was stirred for 3 hr and then treated with 120 μl of glacial acetic acid. The mixture was stirred for an additional 5 min and then poured into 100 ml of water and extracted with pentane. The pentane extracts were washed with water and dried over sodium sulfate. The residue obtained after removal of the pentane was treated with a small portion of pentane and the insoluble iron carbonyl compounds[5] were removed by filtration. The crude product obtained after evaporation of the solvent was purified by preparative tlc (alumina, benzene) giving 119 mg (77%) of decanal, 2,4-DNP mp 104–105°.

We are exploring the possibility that the iron dianion **1** might prove to be a versatile reagent for practical organic synthesis. Further application of the concepts described herein has led to the preparation of carboxylic acid derivatives and ketones. These will be described in subsequent papers.

Acknowledgment. The author thanks Professor J. P. Collman for many stimulating discussions and for support of this research through funds obtained from the National Science Foundation, Grant No. GP 9101. We also thank Professor W. S. Johnson for supplying the 5-bromo-2-methyl-2-pentene.

[10] A referee has suggested that the presence of toluene might arise from homolytic cleavage of the benzyl iron complex **2**, giving benzyl radicals which are abstracting hydrogen from THF. This possibility seems unlikely, since appreciable amounts of toluene are not observed until after the reaction mixture is quenched with acetic acid.

[11] W. B. Renfrow, Jr., and C. R. Hauser, "Organic Synthesis," Coll. Vol. *II*, Wiley, New York, N. Y., 1943, p 607.

[12] (a) Iron pentacarbonyl was obtained from Pressure Chemical Co., Pittsburgh, Pa. (b) While iron pentacarbonyl is much less toxic than nickel tetracarbonyl, it should be handled with caution in an efficient hood.

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Ketonization of Enols in Aprotic Solvents. Photoelimination of β-Keto Sulfides

Sir:

We wish to present evidence that phenacyl alkyl sulfides **1** photolyze by an intramolecular or type II process to give the enol of acetophenone **2** and a thiocarbonyl compound as the primary photoproducts (Scheme I). Of particular interest is the observation that photolysis of phenacyl methyl-d_3 sulfide results in extensive scrambling of the label in the parent ketone and in the product acetophenone, suggesting that the enol **2** is converted to acetophenone **3** by reaction with another molecule of ketone, **1** or **3** (Scheme II).

Certain β-keto sulfides having hydrogens γ to the carbonyl function are reported to undergo quantitative conversion to ketones on photolysis in benzene or chloroform,[1,2] and a mechanism of photoelimination by type II cleavage similar to that observed in the photochemistry of alkanones[3] has been suggested.[1,2,4] Sulfur should by this mechanism eliminate as a thiocarbonyl compound, but has not hitherto been detected, presumably because thioaldehydes and thioketones are unstable and readily photolyze and/or polymerize. β-Keto sulfides that do not possess γ hydrogens are reported to give disulfides by homolysis of a carbon–sulfur bond,[5] and a related mechanism can be written for the photolysis of β-keto sulfides of type **1** (eq 1).

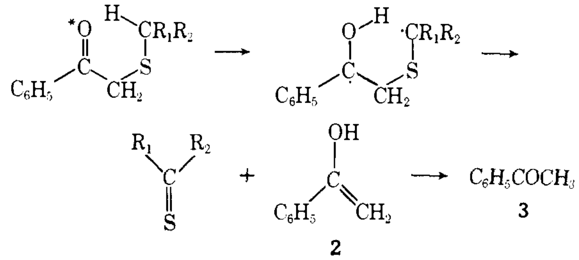
$$\underset{\mathbf{1}}{C_6H_5COCH_2SCH_3} \xrightarrow{h\nu} C_6H_5CO\dot{C}H_2 + \dot{S}CH_3 \longrightarrow C_6H_5COCH_3 + (S{=\!=}CH_2)_x \quad (1)$$

The present work was in fact initiated in the hope of distingushing between an intramolecular mechanism (Scheme I) and an intermolecular mechanism (eq 1) in the photolysis of **1**. We have found that the photolysis of phenacyl methyl sulfide (**1a**) in deuteriochloroform does *not* lead to the incorporation of deuterium in the acetophenone produced (Table I, runs 1 and 2), and a mechanism of photolysis involving homolysis of the phenacyl carbon–sulfur bond (eq 1) is therefore unlikely since abstraction of deuterium from the solvent would be expected to occur to some extent.

Scheme I

$$C_6H_5COCH_2SCHR_1R_2 \xrightarrow[n\rightarrow\pi^*]{h\nu}$$

1a, $R_1 = R_2 = H$
1b, $R_1 = CH_3, R_2 = C_6H_5$
1c, $R_1 = CH_3, R_2 = H$



Solutions of phenacyl 1-phenylethyl sulfide (**1b**), 0.5 *M* in benzene or chloroform, on photolysis[6] became intensely colored within minutes (λ_{max} 560 nm). After 3 hr, photolysis of **1b** was complete and two volatile

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[1] H. Hogeveen and P. J. Smit, *Recl. Trav. Chim. Pays-Bas.*, **85**, 489 (1966).

[2] R. H. Fish, L. C. Chow, and M. C. Caserio, *Tetrahedron Lett.*, 1259 (1969).

[3] (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 382–385; (b) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967); (c) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).

[4] B. M. Trost, *ibid.*, **89**, 138 (1967).

[5] J. R. Collier and J. Hill, *Chem. Commun.*, 700 (1968); 640 (1969).

[6] A 200-W Hanovia lamp Type S was used with a Pyrex filter. A 550-W lamp with a Corning 0-51 filter was also effective.

Table I. Mass Spectral Data for Acetophenone Obtained from the Photolysis of Phenacyl Methyl Sulfide

Run	Reactant[a]	Solvent	Time, hr[b]	*m/e*[c] 120+	121+	122+	123+	124+
1	$C_6H_5COCH_2SCH_3$	$CHCl_3$[d]	17	100[e]	9.5[e]	0.9[e]		
2	$C_6H_5COCH_2SCH_3$	$CDCl_3$[d]	17	100	9.5	0.9		
3	$C_6H_5COCH_2SCD_3$	$CHCl_3$[d]	17	100	75.1	22.3	3.0	
4	$C_6H_5COCH_2SCD_3$	C_6H_6	4	100	74.5	14.3	1.3	
5	$C_6H_5COCH_2SCD_3$	C_6H_6	17	100	79.6	18.0	2.4	
6	$C_6H_5COCH_3$ +	C_6H_6	4	100[g]	10.0[g]	5.1[g]	55.0[g]	5.0[g]
	$C_6H_5COCD_3$[f] (2:1)			100	10.0[h]	5.3[h]	55.0[g]	5.0
7	$C_6H_5COCH_3$ +	C_6H_6	18	100[g]	10.1[g]	5.6[g]	53.3[g]	5.1[g]
	$C_6H_5COCD_3$[f] (2:1)			100	10.0[h]	5.2[h]	53.3	5.1
8	$C_6H_5COCH_3$ +	C_6H_6	18[i]	100[g]	10.4[g]	5.3[g]	54.9[g]	4.3[g]
	$C_6H_5COCD_3$[f] (2:1)			100	10.0[h]	5.3[h]	54.9	4.3
9	$C_6H_5COCH_2SCH_3$ +	C_6H_6	2	100[g]	19.2[g]	20.8[g]	90.0[g]	8.4[g]
	$C_6H_5COCD_3$ (1:1)			100	10.4[h]	9.3[h]	90.0	8.4
10	$C_6H_5COCH_2SCD_3$[j]	C_6H_6	4	100[j]	29.6[j]	8.6[j]		
11	$C_6H_5COCH_2SCD_3$			100[k]	11.4[k]	5.4[k]		

[a] 0.6 *M*. [b] Duration of photolysis. [c] Values are relative to *m/e* (120) as 100. [d] Ethanol free. [e] Theoretical values are 100:8.8:0.54. [f] Prepared from methyl-d_3-lithium and lithium benzoate in dry ether; *m/e* values for molecular ion were 121:122:123:124 = 0:2.2:8.7:100: 9.2, indicating 2% $C_6H_5COCH_2D$, 8% $C_6H_5COCHD_2$, and 90% $C_6H_5COCD_3$. [g] Experimental values. [h] Calculated values based on known relative intensities of 120:121:122 for $C_6H_5COCH_3$ and 121:122:123:124 for $C_6H_5COCD_3$ listed in footnotes *e* and *f* assuming no exchange. [i] Control run maintained in dark. [j] **1a**-d_3 recovered after 63% conversion; the *m/e* values are for the molecular ion of **1a**-d_x 169:170:171. [k] *m/e* values are for **1a**-d_3 before photolysis; theoretical values for isotopically pure material are 169:170:171 = 100:10.7:5.1.

products were shown to be present by glpc and nmr. The crude reaction mixture showed aromatic proton resonances and *two* singlets at 2.50 and 3.00 ppm in chloroform (2.13 and 2.56 ppm in benzene). These were identified, respectively, as the methyl resonances of acetophenone and *thioacetophenone*[7] by comparison with authentic samples.[10] The yield was quantitative. To our knowledge, this is the first reported example where the thiocarbonyl product inferred in the photolysis of β-keto sulfides of type **1** has been positively identified. Thioacetophenone produced in the photolysis of **1b** is relatively stable to 3240-Å light, but rapidly decolorizes on exposure to air and to light of shorter wavelengths. In striking contrast to the photolytic behavior of the analogous β-keto ethers,[13] no thietanol formation was noted on photolysis of β-keto sulfides **1**.

Photolysis of phenacyl methyl-d_3 sulfide[14] in chloroform or benzene gave acetophenone with significant incorporation of deuterium (Table I, runs 3–5). According to Scheme I, the expected product is $C_6H_5COCH_2D$, but the *m/e* values of Table I show that *the label is intermolecularly scrambled.* Approximately 54.4, 36.1, 8.7, and 0.7% of acetophenone-d_0, -d_1, -d_2, and -d_3 were obtained in chloroform with overall 0.65 g-atom of deuterium incorporated per mole of acetophenone. Most unexpected, however, was the observed incorporation of deuterium into unreacted **1a**-d_3 (Table I, runs 10 and 11). While related studies of type II photoelimination of γ-deuterium-labeled alkanones in the *gas phase* are similarly reported to give significant loss and scrambling of the label in the product ketone,[15,16] no exchange was noted in the parent alkanones, and the observed scrambling was ascribed to enol–ketone transformation by way of a wall reaction[17] and/or reaction between two enol molecules.[16] The present data indicate that, in aprotic solvents, the lifetime of **2** is appreciable and that *a major route for enol–ketone transformation involves reaction between enol and ketone* (Scheme II) since photolysis of **1a**-d_3 led to **1a**-d_4 and **1a**-d_5 as well as acetophenone-d_0, -d_1, -d_2, and -d_3. That acetophenone may also function to ketonize the enol was determined from the photolysis of **1a**-d_0 in the presence of acetophenone-d_3 which led to formation of significant amounts of acetophenone-d_1 and -d_2 (Table I, run 9).

Alternate scrambling mechanisms include deuterium exchange between two molecules of ketone. However, 2:1 mixtures of acetophenone-d_0 and -d_3 in benzene did not give acetophenone-d_1 or -d_2 either in the dark or on irradiation for 4–18 hr (Table I, runs 6–8). Also, exchange between **1a** and acetophenone-d_3 in the ground state did not occur in benzene solution. Exchange between acetophenone and steady-state concentrations of ground- or excited-state thioformaldehyde is considered improbable for the reason that a 1:1:1 mixture of acetophenone-d_0 and -d_3 and thioacetophenone-d_0 in benzene did not incorporate deuterium into thioacetophenone or scramble deuterium in acetophenone either in the dark or on irradiation.[18]

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(7) The downfield shift of the methyl resonance of thioacetophenone relative to that of acetophenone is consistent with greater anisotropy of the thiocarbonyl group[8] and greater bond polarity.[9]

(8) S. McKenzie and D. H. Reid, *Chem. Commun.*, 401 (1966).

(9) See E. Campaigne in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., 1966, pp 934–935.

(10) Thioacetophenone was synthesized by a published procedure:[11] bp, 89–92° (8 mm) [lit. 97–100°, (12 mm)]; nmr, five-proton multiplet near 7 ppm and three-proton singlet at 3.1 ppm in CCl_4; visible spectrum, λ_{max} 573 nm in cyclohexane.[12]

(11) R. Mayer and H. Berthold, *Chem. Ber.*, **96**, 3096 (1963); R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem., Int. Ed. Engl.*, **3**, 277 (1964).

(12) J. Fabian, H. Viola, and R. Mayer, *Tetrahedron*, **23**, 4323 (1967).

(13) F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970); R. B. LaCount and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1965).

(14) Prepared by the following reactions

$$CD_3I + (NH_2)_2C{=}S \longrightarrow (NH_2)_2C{=}\overset{+}{S}CD_3I^- \xrightarrow{KOH}$$

$$CD_3SH \xrightarrow[2.\ C_6H_5COCH_2Br]{1.\ NaOCH_3} C_6H_5COCH_2SCD_3$$

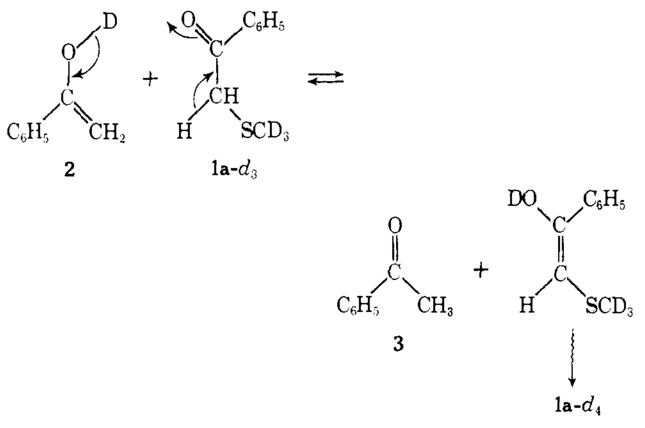
(15) J. R. McNesby and A. S. Gordon, *J. Amer. Chem. Soc.*, **80**, 261 (1958).

(16) R. Srinivasan, *ibid.*, **81**, 5061 (1959).

(17) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *ibid.*, **86**, 3602 (1964).

(18) A 550-W lamp was used with a Corning 3-74 filter to selectively excite the thiocarbonyl chromophore.

Scheme I



The nature of the excited state in the photolysis of **1a** and **1b** is not known, but it may be noted that if the triplet excited state is involved it must be very short-lived, since quenching by either oxygen or thioacetophenone was not observed.

(19) This work was supported by the National Science Foundation under Grant No. NSF-GP-12828.

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The Photochemistry of Bicyclo[3.2.0]hept-3-en-2-ones. Formation of 2-Cyclohexenecarboxylic Acid Derivatives[1]

Sir:

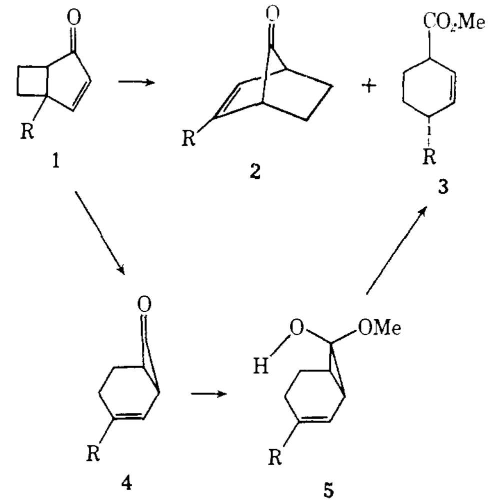
We have previously shown that irradiation of bicyclo[3.2.0]hept-3-en-2-one (**1a**) in pentane or in methylene chloride yields dimer(s) and 7-ketonorbornene **2a** and that the latter is formed *via* a nonconcerted path.[2] In this communication we report the conversion of bicycloheptenones **1a,b** into the methyl 2-cyclohexenecarboxylates **3a,b** as well as evidence which indicates the intermediacy of a cyclopropanone in this transformation.

Irradiation of **1a** (0.0672 *M* in methanol) gave **2a** (and the corresponding ketal), dimer(s), and **3a** (10–15%).[3] Identification of ester **3a** is based on its hydrogenation to methyl cyclohexanecarboxylate coupled with its nmr spectrum, which shows the presence of two vinyl hydrogens and differs from that of methyl 3-cyclohexenecarboxylate. Irradiation of **1b** (0.0156 *M* in methanol) gave **2b**, dimers, and **3b** (∼15%). Ester **3b** was identified by comparison with an authentic sample of methyl *trans*-4-methyl-2-cyclohexenecarboxylate obtained from reduction of *p*-toluic acid.[4] No cis ester could be detected in the gas chromatogram of the product.

That esters **3a,b** do not arise from the 7-ketonorbornenes **2a,b** is inferred from the fact that (a) irradiation of **2a** in pentane or in methanol under the above conditions yields only recovered **2a**, and (b) addition of methanol to **2b** should give methyl 2- or 3-methyl-2-cyclohexenecarboxylate rather than **3b**. The stereospecific formation of **3b** is inconsistent with the intermediacy of a monocyclic ketene.

Irradiation of **1b** in deuteriomethanol containing a trace of deuteriosulfuric acid followed by dilution with ordinary water, extraction with pentane, and isolation by preparative glpc gave **3b** containing no deuterium (<5%).[6] Irradiation in ordinary methanol containing a trace of ordinary sulfuric acid, dilution with deuterium oxide, and isolation as above gave **3b** containing 23% of one deuterium at C-4, as evidenced by mass spectroscopy and partial collapse of the doublet at δ 0.97 to a singlet. These results require the intermediacy of a species containing one readily exchangeable hydrogen and may be accommodated in the following scheme: photoisomerization of **1** to the cyclopropanone **4**, immediate conversion of **4** to hemiketal **5** (attack on the less crowded face of the cyclopropanone),[7] and thermal isomerization of the hemiketal to the observed ester **3**.[8]

Efforts to firmly establish the intermediacy of **4** by irradiation of **2b** in pentane followed by addition of methanol and work-up, or by infrared spectroscopy using the technique of Chapman,[9] have been unsuccessful. Our efforts to isolate adducts of **4** are continuing.



a, R = H
b, R = CH_3

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[1] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank the National Science Foundation for a grant toward the purchase of the mass spectrometer used in this work.

[2] R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Amer. Chem. Soc.*, **92**, 3809 (1970).

[3] (a) Changing the irradiation solvent from pentane to methanol had no significant effect on the yields of 2 and dimer. (b) These irradiations were carried out with a Hanovia 450-W mercury arc or with "blacklights" in Pyrex vessels and were worked up by dilution with water, extraction with pentane, drying, solvent distillation, and preparative glpc. The isolated yield of 3a was 8.5%.

[4] The details of this two-stage reduction (lithium-ammonia) will be described in a full paper. Both cis and trans isomers of 3b are obtained and are separable. Assignment of stereochemistry is based on catalytic hydrogenation of 3b to the known *trans*-4-methylcyclohexanecarboxylic acid.[5]

[5] A. A. B. Kleis, A. A. Massier, D. Medema, P. E. Verkada, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **80**, 595 (1961).

[6] Irradiation of 1b in methanol containing sulfuric acid followed by the described work-up gave 2b, 3b, and dimer(s) in the same yields obtained in the absence of the acid.

[7] N. J. Turro, *Accounts Chem. Res.*, 2, 25 (1969).

[8] The analogous intramolecular hydrogen transfer in the carene series, $\Delta H^{\ddagger}$ 27 kcal/mol, $\Delta S^{\ddagger}$ −17 eu, has been discussed: (a) G. Ohloff, *Tetrahedron Lett.*, 3795 (1965); (b) K. Gollnick, *ibid.*, 327 (1966); and K. Gollnick and G. Schade, *Tetrahedron*, 22, 123 (1966).

[9] L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Amer. Chem. Soc.*, 91, 3664 (1969). Chapman has noted the rapid photodecarbonyla-