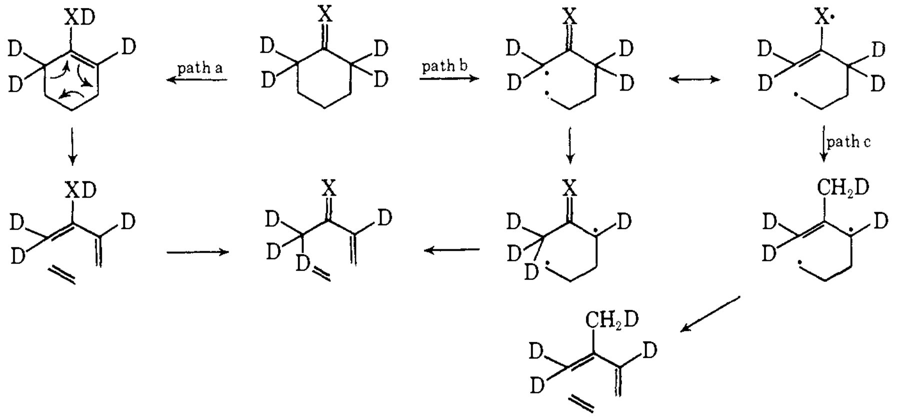
Scheme I



1,3-butadiene (3), 1,5-hexadiene (3), cyclopentane (3), cyclopentadiene (2), acrolein (2), and benzene (1). The thermal stability of the products at 1050° was not extensively examined, but it was found that MVK itself decomposed to the extent of about 50% to give all the products observed from cyclohexanone except the last four.

In order to ascertain the primary thermal process involved, three specifically deuterated cyclohexanones were prepared and thermolyzed. The deuterium distribution in some of the products was obtained and part of the results are summarized in Table I.

Cyclohexanone-*2,2,6,6-d_4* gave MVK with 93% overall retention of deuterium. The fragmentation spectrum clearly showed the presence of the retained deuterium in the methyl group. The deuterium content of the MVK from cyclohexanone-*3,3,5,5-d_4* was half that of the starting material, while essentially no deuterium was present in the MVK from cyclohexanone-*4-d*.

The observations require that, following β cleavage, a hydrogen atom (or ion) α to the carbonyl be intramolecularly transferred to the other α position. Two mechanisms, at least, can be envisaged (Scheme I). One (path a, X = O) requires prior enolization, perhaps on the walls, followed by a reverse Diels–Alder reaction and subsequent ketonization. The second (path b, X = O) involves initial homolysis of the β carbon–carbon bond, hydrogen atom migration, and collapse of the 1,4 biradical in the expected manner (or *vice versa*). Relevant evidence was obtained as follows. Thermolysis of methylenecyclohexane-*2,2,6,6-d_4* gave isoprene, the equivalent of MVK in this system, in 12% yield with 87.4% total deuterium retention. Path a ($X = CH_2$) is evidently inapplicable[8] here, and path b (and path c) must be operative. In view of the parallel results we favor, but essentially by analogy, the view that path b (X = O) be that followed in MVK formation.

The results permit a quantitative check. The mechanism demands that equimolar amounts of ethylene and MVK be formed, but analysis was complicated by the fact that the decomposition of MVK also produced ethylene. The monodeuterated ethylene produced from cyclohexanone-*4-d_1* gave the amount of ethylene formed by path b (X = O) as 63%. There should be the amount of unlabeled ethylene from the *2,2,6,6-d_4* material:[9] the observed value was 64.5%. Since the total isolated yield of ethylene was actually 85% then the actual yield of MVK (equivalent to unlabeled ethylene) may be computed at 54%, *i.e.*, a figure about twice the actual yield, but in good agreement with the 50% recovery of MVK under the same conditions in the control experiment mentioned earlier.

The β cleavage to give MVK is thus the major pathway followed in cyclohexanone thermolysis. It represents a minimum of the total β-cleavage products, and reveals this fission as the primary thermal process.[10,11]

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[8] To follow this route prior rearrangement to methylcyclohexene would be required. Since <0.1% of this hydrocarbon was obtained from the thermolysis of methylenecyclohexene this explanation would require the complete decomposition of methylcyclohexene under these conditions. Experimentally, it was found that about 15% of methylcyclohexene was recovered in the thermolysis of this substance, together with about 50% isoprene.

[9] Any ethylene from MVK should surely have contained at least one deuterium atom.

[10] Crandall has suggested such a cleavage in his study of the photolysis and thermolysis of cyclooct-4-enone: J. K. Crandall, J. P. Arrington, and R. J. Watkins, *Chem. Commun.*, 1052 (1967).

[11] The thermolysis of cyclopentanone has been reported to give α-cleavage products resembling those of photochemical fission (F. M. Delles, L. T. Dodd, L. F. Lowden, F. J. Romano, and L. G. Daignavet, *J. Amer. Chem. Soc.*, **91**, 7645 (1969)). We intend to study this substance under our conditions.

[12] Holder of N.R.C. Scholarship, 1967–present.

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Facile Conversion of Alkyl Bromides into Aldehydes Using Sodium Tetracarbonylferrate(−II)

Sir:

We wish to report that the d^{10} dianion derived from iron pentacarbonyl is an effective reagent for the conversion of primary bromides into corresponding aldehydes containing an additional carbon atom. Reduction of iron pentacarbonyl in THF by sodium amalgam followed by treatment of the resulting dianion, sodium tetracarbonylferrate(−II)[1] (**1**), with primary bromides in the presence of triphenylphosphine at 25° gives, after quenching with acetic acid, the corresponding aldehyde in high yield.[2] Results using typical alkyl bromides are

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[1] V. W. Hieber and G. Braun, *Z. Naturforsch.*, **146**, 132 (1959).

[2] (a) Aromatic aldehydes have been obtained previously by the reaction of aryllithium reagents with iron pentacarbonyl; see M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, 37, 341 (1964). (b) It

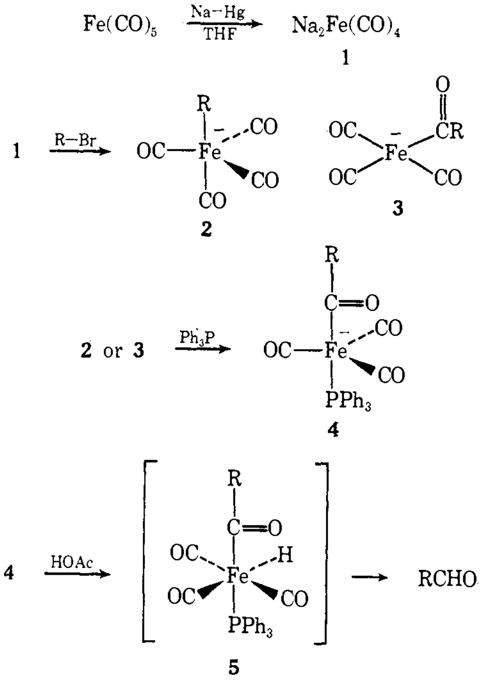
Table I. Conversion of Alkyl Bromide into Aldehydes

Alkyl bromide[a]	$Fe(CO)_5/RBr$	Ph_3P, mmol	Reaction time, hr	Product[b]	Yield, %[c]
$CH_3(CH_2)_4Br$	1.38	1.20	3	$CH_3(CH_2)_4CHO$	99 (86[d])
$CH_3(CH_2)_8Br$	1.40	1.20	3	$CH_3(CH_2)_8CHO$	91 (80,[d] 77[e])
$PhCH_2CH_2Br$	1.38	1.20	3	$PhCH_2CH_2CHO$	86[f]
$C_6H_{11}CH_2Br$	1.38	1.20	3	$C_6H_{11}CH_2CHO$	96 (85,[d] 75[e])
$(CH_3)_2C{=}CH(CH_2)_2Br$	1.38	1.20	3	$(CH_3)_2C{=}CH(CH_2)_2CHO$	81
$CH_3(CH_2)_5CHBrCH_3$	2.0	1.20	48	$CH_3(CH_2)_5CH(CH_3)CHO$	50[g]

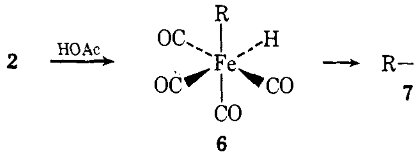
[a] All reactions reported here were conducted with 1.00 mmol of alkyl bromide. [b] All aldehydes were identified by spectral properties and by comparison with authentic samples. [c] Yields determined by glpc analysis using an appropriate internal standard previously calibrated against an authentic sample of pure aldehyde. [d] Yield determined as the 2,4-DNP derivative of the aldehyde after work-up. [e] Isolated yield after purification by preparative tlc. [f] Styrene identified as a minor product. [g] Isomeric octenes identified as by-products.

shown in Table I. This procedure embodies several fundamental mechanisms of organotransition-metal chemistry: oxidative addition, migratory insertion, and reductive elimination.[3]

It is suggested that oxidative addition of the alkyl bromide to the coordinatively saturated iron dianion **1** affords the saturated alkyl iron anion **2**, which may be in equilibrium with the unsaturated acyl iron anion **3**. Addition of a ligand such as triphenylphosphine converts the intermediate (**2** or **3**) into the saturated phosphine-substituted acyl iron anion **4**.[4] Protonation of anion **4** by acetic acid is presumed to give the intermediate acyl iron hydride **5** which undergoes reductive elimination to yield the aldehyde and a mixture of triphenylphosphine-substituted iron carbonyl complexes.[5]



Support for this sequence is derived from the observation that in the absence of added triphenylphosphine the major product of the reaction is the alkane **7** and a small amount of the aldehyde. The alkane apparently arises through protonation of anion **2** followed by reductive elimination of the alkane from the intermediate alkyl iron hydride **6**, while the aldehyde reflects either the presence of some unsaturated acyl anion **3** in equilibrium with **2** or the ability of CO remaining in the solution as a by-product of the reduction to function as a ligand. When 1-bromononane was treated with a solution of the dianion **1** which had been swept with N_2 the yield of aldehyde was reduced to 13% and a 50% yield of nonane was obtained. Under an atmosphere of CO hexanal was obtained in 75% yield from the reaction of amyl bromide with **1**.



While sodium tetracarbonylferrate(–II) is an effective reagent for the conversion of primary bromides into homologous aldehydes, secondary bromides are less satisfactory. Treatment of the dianion **1** with 2-bromooctane in the presence of triphenylphosphine, followed by quenching with acetic acid, gave the expected aldehyde, 2-methyloctanal, in 50% yield, along with a significant amount of octenes. Since oxidative addition involving alkyl halides is equivalent to nucleophilic substitution at carbon,[6] secondary halides would be expected to react more slowly and to be subject to E2 elimination in the presence of the strongly basic dianion.[7,8]

Benzylic bromides likewise give poor yields of aldehydes. Treatment of the dianion **1** with benzyl bromide at –78°, followed by quenching with acetic acid at 25°, gave toluene as the major product along with a small amount of phenylacetaldehyde. The predomi-

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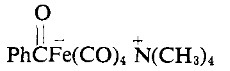
has been reported that ethanolic solutions of tetracarbonylferrate(–II) salts react with epoxides to give β-hydroxy esters and with *n*-propyl iodide to give a mixture of ethyl *n*-butyrate and *n*-butyraldehyde; see Y. Takegami, Y. Watanabe, T. Mitsudo, and H. Masada, *Bull. Chem. Chem. Jap.*, **42**, 202 (1969); (c) Y. Takegami, Y. Watanabe, and H. Masada, *ibid.*, **40**, 1459 (1967).

[3] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

[4] An analogous acyl iron anion i has been obtained as its tetramethylammonium salt from the addition of phenyllithium to iron penta-



$$Ph\overset{O}{\overset{\|}{C}}\overset{-}{Fe}(CO)_4\ \overset{+}{N}(CH_3)_4$$

i

carbonyl: E. O. Fischer, V. Kiener, and R. D. Fischer, *J. Organometal. Chem.*, **16**, P60 (1960).

[5] Infrared analysis of the isolated iron carbonyl complexes indicated the presence of $Fe(CO)_4Ph_3P$ and $Fe(CO)_3(Ph_3P)_2$.

[6] (a) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970); (b) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **91**, 4313 (1969); (c) F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **92**, 1414 (1970).

[7] J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1956, p 180.

[8] $H_2Fe(CO)_4$ has $pK_{a_1} = 4.4$, $pK_{a_2} = 13.4$.[9]

[9] P. Krumholz and H. M. A. Stettiner, *J. Amer. Chem. Soc.*, **71**, 3035 (1949).

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.

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(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:

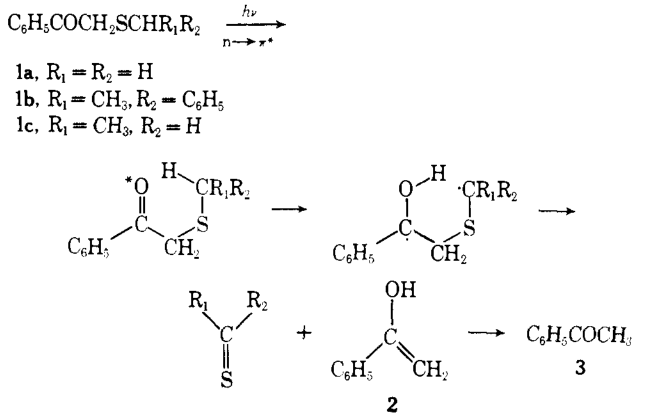
We wish to present evidence that phenacyl alkyl sulfides **1** photolyze by an intramolecular or type II process to give the enol of acetophenone **2** and a thiocarbonyl compound as the primary photoproducts (Scheme I). Of particular interest is the observation that photolysis of phenacyl methyl-d_3 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



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.