# Formation of Ketones in the Oxo Synthesis

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Ketones have been prepared by the reaction of hydrogen tetracarbonylcobaltate(−I) with monoolefins, conjugated and unconjugated diolefins. A mechanism is proposed for ketone formation in which only the last step of the hydroformylation mechanism for aldehyde formation has been changed from the decomposition involving hydrogen tetracarbonylcobaltate(−I) to one involving alkyl tetracarbonylcobaltate(−I).

Although the preparation of aldehydes from olefins and hydrogen tetracarbonylcobaltate(−I) in a stoichiometric reaction or a catalytic process is well-known, the preparation of ketones by such reactions is rare. Ketones have been observed as a major product when ethylene is subjected to oxo conditions and as a minor product when other olefins have been used.[2] In a reaction which would seem related, although it does not involve an olefin, Hieber[3] observed acetone in the decomposition of methyl tetracarbonylcobaltate(−I). While studying the coordination compounds formed by diolefins and hydrogen tetracarbonylcobaltate(−I), considerable amounts of oxygenated organic compounds were observed in several cases. Since identification of these compounds indicated that some were ketones, it was decided to investigate further the possibility of preparing ketones by such reactions.

## Results and Discussion

Reactions were carried out by adding the olefin to an aqueous solution of potassium tetracarbonylcobaltate(−I) in an autoclave and then acidifying to produce hydrogen tetracarbonylcobaltate(−I). With conjugated diolefins, temperatures above 120° were necessary to decompose the somewhat stable complexes, substituted π-allyl tricarbonylcobaltates. With unconjugated diolefins, room temperature was sufficient; monoolefins at room temperature gave only aldehydes. At lower temperatures in pentane solvent, 1-butene gave predominantly ketones as oxygenated product.

The mechanism of aldehyde formation recently has been discussed by various workers.[4-7] Although there are several points of disagreement, the following sequence of reactions is compatible with available data.

$$\mathrm{RCH{=}CH_2 + HCo(CO)_4 = RCH_2CH_2Co(CO)_4}$$

$$\mathrm{RCH_2CH_2Co(CO)_4 = RCH_2CH_2COCo(CO)_3}$$

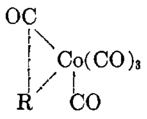
$$\mathrm{RCH_2CH_2COCo(CO)_3 + CO = RCH_2CH_2COCo(CO)_4}$$

$$\mathrm{RCH_2CH_2COCo(CO)_3 + HCo(CO_4 = RCH_2CH_2CHO + CO_2(CO)_7}$$

The sequence is written for only one of the isomeric aldehyde products.

Acyl compounds, such as the one above, have been prepared by Heck and Breslow.[8,9]

The second and third steps may proceed by a concerted carbonyl insertion mechanism involving the following transition state.[4,10,11]



The entering carbon monoxide molecule attaches itself to cobalt while one of the original carbon monoxide ligands forms the acyl group.[12] Such a mechanism would eliminate the coordinately unsaturated acyl tricarbonylcobaltate(−I), and the last step would become the following.[1b,2]

$$\mathrm{RCH_2CH_2COCo(CO)_4 + HCo(CO)_4 = RCH_2CH_2CHO + Co_2(CO)_8}$$

The mechanism proposed by Heck and Breslow[4] would involve $HCo(CO)_3$ and appears less likely in view of a mass spectrometric analysis of hydrogen tetracarbonylcobaltate(−I) which showed no hydrogen-containing fragments.[13]

The formation of ketones can be explained by a mechanism similar to the one above by assuming that the alkyl tetracarbonylcobaltate(−I) of step 1 can function in the same way as hydrogen tetracarbonylcobaltate(−I) in the decomposition that follows

$$\mathrm{RCH_2CH_2COCo(CO)_{\mathit{x}} + R'Co(CO)_4 \longrightarrow RCH_2CH_2CR'O + Co_2(CO)_{4+\mathit{x}}}$$

where $x$ is 3 or 4, depending on which mechanism is preferred, and R′ is $RCH_2CH_2$– or H. Since the decomposition would proceed through an intermediate or activated complex, steric factors would strongly favor R′ = H. However, the alternate reaction should become important when (1) R is small (R = H for ethylene), (2) the concentration of $HCo(CO)_4$ is low, or (3) the two reactants are held together (that is, an *intra*molecular decomposition).

Furthermore, the same decomposition can account for the formation of acetone from methyl tetracarbonylcobaltate(−I).[1a]

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(1)(a) Esso Research Laboratories, Baton Rouge, La.; (b) University of Bergen, Norway.

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(5) C. W. Bird, *Chem. Rev.*, 283 (1962).

(6) M. A. Bennett, *ibid.*, 611 (1962).

(7) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(8) R. F. Heck and D. S. Breslow, *Chem. Ind.* (London), 467 (1960).

(9) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

(10) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

(11) K. A. Keblys and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

(12) T. H. Coffield, R. D. Closson, and J. Kozikowski, Abstracts of Conference Papers, Intern. Conf. on Coordination Chemistry, London, April 6–11, 1959, Paper No. 26, p. 126.

(13) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 2717 (1953).

$$CH_3Co(CO)_4 \rightleftharpoons CH_3COCo(CO)_3$$

$$CH_3Co(CO)_4 + CH_3COCo(CO)_3 \rightleftharpoons CH_3COCH_3 + Co_2(CO)_7$$

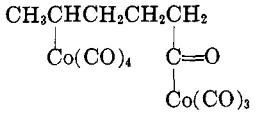
As no $HCo(CO)_4$ is present, the above is the only decomposition.

As mentioned previously, use of ethylene in an oxo reaction leads to considerable yield of ketone; with longer-chain olefins, ketone becomes only a minor by-product.

In the present study, when a large excess of butene-1 reacted with hydrogen tetracarbonylcobaltate(−I) at room temperature, only aldehyde product was isolated; when the reactants were mixed at −8° and then heated, about 90% of the oxygenated product was ketone. The low temperature mixing would favor formation of intermediates, both alkyl and acyl, and would use up the hydrogen tetracarbonylcobaltate(−I) before the decomposition reaction. The decomposition reaction would then involve the alkyl and acyl intermediates and result in ketone formation.

The reaction of 1,4-pentadiene at room temperature yielded a mixture of 5-hexenal (8% yield), 2-methylcyclopentanone (22% yield), and coordination compounds (3% yield). A small amount of cyclohexanone also was noted. The coordination compounds have been identified as isomers (*syn-* and *anti-*) of π-(1-ethylallyl)-tricarbonylcobaltate(−I).[14]

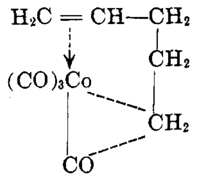
The formation of 5-hexenal would follow the usual aldehyde mechanism, with only one double bond being used. Under conditions which regenerate the hydrogen tetracarbonylcobaltate(−I), the other double bond would be expected to react as well; these reactions were carried out with a 1:1 mole ratio of hydrogen tetracarbonylcobaltate(−I) and diolefin. By the mechanism proposed, the cyclic ketone would result from formation of the alkyl and acyl intermediates within the same molecule.



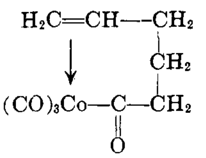
$$CH_3\underset{\displaystyle Co(CO)_4}{\underset{|}{CH}}CH_2CH_2\underset{\displaystyle \underset{\displaystyle Co(CO)_3}{\underset{|}{C{=}O}}}{\underset{|}{CH_2}}$$

Owing to proximity of reactants, the ketone reaction would compete favorably with the aldehyde reaction.

An alternate scheme can explain the formation of ketone from diolefins. Starting with the intermediate $CH_2{=}CHCH_2CH_2CH_2Co(CO)_4$, the next step would be a cyclic transition state.

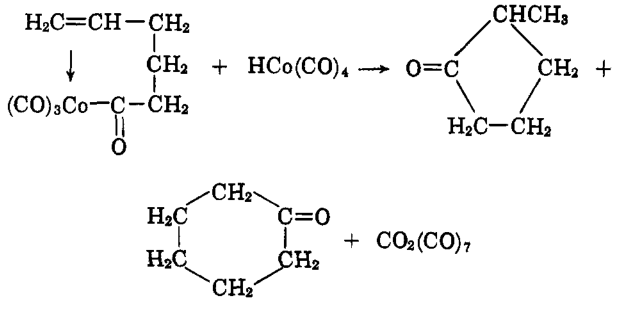


This transition state would yield the following complex.



Existence of such π-complexes at lower temperature has indeed been demonstrated by Heck.[15]

This intermediate presumably would be sufficiently stable to exist long enough for a hydrogen tetracarbonylcobaltate(−I) to interact with it, thus giving a cyclic ketone.



The predominance of the 2-methylcyclopentanone can be explained on the basis of the cyclic intermediate, which favors a closer approach of the carbonyl group to C-5 rather than to C-6 of the ring.

The reaction of 1,3-butadiene yielded, on decomposition of the complex at 120°, both saturated and unsaturated $C_9$ ketones. Only straight-chain ketones were observed; furthermore, when a similar reaction was carried out under a pressure of carbon monoxide only, the saturated 5-nonanone was obtained. Formation of ketone could proceed again through alkyl and acyl intermediates, formed from the π-complex under the reaction conditions. The alternate scheme is unlikely, since hydrogen tetracarbonylcobaltate(−I) probably is used up in forming the stable complex.

## Experimental

**1,4-Pentadiene Reaction.**—A solution of 0.2 mole of potassium tetracarbonylcobaltate(−I) in 300 ml. of water was placed in a 1-l. steel autoclave, 120 ml. of concentrated phosphoric acid and 0.2 mole of 1,4-pentadiene were added without mixing, and the autoclave was closed, inverted to mix the reactants, and rocked for 24 hr. The vessel was opened under a stream of nitrogen and 100 ml. of hexane was added to extract the products. The hexane layer was separated, washed with distilled water, dried over sodium sulfate, and transferred to a distillation apparatus. The hexane was removed by aspirator vacuum; the product was distilled under high vacuum. The material distilling below 45° (1 mm.) was collected as one fraction; the material distilling at 45° was predominantly π-(1-ethylallyl)tricarbonylcobaltate(−I).

The first fraction was further separated into two pure compounds in a Beckman Megchrom gas chromatograph equipped with a silicone rubber column. The first component (8% yield) was identified as 5-hexenal. The infrared spectrum showed absorptions indicative of aldehyde and terminal unsaturation, and absorptions indicative of branching (methyl) were absent. The molecular weight of 98 (mass spectrum) checked for 5-hexenal. The 2–4 dinitrophenylhydrazone isolated according to the procedure of Kharasch, *et al.*,[16a] had m.p. 103°, lit.[16a] m.p. 103°; a mixture melting point with an authentic sample showed no depression.

The second component (22% yield) was identified as 2-methylcyclopentanone. The infrared spectrum was identical with that of an authentic sample and the phenylhydrazone melted at 60° dec., lit.[16c] m.p. 60° dec. A mixture melting point with the authentic phenylhydrazone showed no depression.

**1,3-Butadiene Reaction.**—A solution of 0.2 mole of potassium tetracarbonylcobaltate(−I) in 300 ml. of water was placed in the autoclave, and 120 ml. of concentrated phosphoric acid and 0.2

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[15] R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3116 (1963).

[16] (a) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1275 (1953). (b) "Dictionary of Organic Compounds," Vol. III, Heilbron Oxford Press, New York, N. Y., 1953; (c) p. 357.

mole of 1,3-butadiene were added without mixing. The autoclave was closed, inverted to mix the reactants, rocked at room temperature for 24 hr., and then heated to 120° for 2 hr. After cooling, the vessel was opened, the product was extracted with hexane, and the hexane layer was washed with distilled water and dried over sodium sulfate. After removing the hexane, the product was separated on the preparative scale gas chromatograph.

The first component (18% yield) was identified as 5-nonanone. The gas chromatographic retention time and infrared spectrum were identical with an authentic sample prepared by the method of Briese and McElvain,[17] and the molecular weight (mass spectrum) was correct for 5-nonanone. The semicarbazone melted at 90°, lit.[16b] m.p. 90°, and showed no depression when mixed with the authentic derivative.

The second compound (9% yield) was identified as 3-nonen-5-one. The infrared spectrum contained adsorptions characteristic of ketone carbonyl and conjugated unsaturation, and the molecular weight (mass spectrum) was 140. Satisfactory elemental analysis was not obtained because of sensitivity to air as reported by Powell and Nielsen.[18] However, hydrogenation of the carbon–carbon unsaturation as described by Powell and Nielsen[18] yielded 5-nonanone. The infrared spectrum was identical with the authentic sample prepared above, the molecular weight (mass spectrum) was 142 (calcd. for 5-nonanone, 142), semicarbazone had m.p. 90° (lit.[16b] m.p. 90°), and mixture melting point of semicarbazone with authentic derivative was 90°.

The above experiment was repeated, and carbon monoxide gas was added to a pressure of 1200 p.s.i. before heating. The product, treated as before, yielded only one major component, 5-nonanone (25% yield), in the gas chromatograph.

In both of the above experiments, minor peaks were observed by gas chromatography but were not separated. These corresponded in retention time to *n*-valeraldehyde, 2-methyl-1-butanal, and vinylcyclohexene.

**1-Butene Reaction.**—Gaseous hydrogen tetracarbonylcobaltate(−I) was prepared by slowly dropping an aqueous solution of potassium tetracarbonylcobaltate(−I) into concentrated phosphoric acid under nitrogen. The acid solution was constantly stirred while nitrogen was bubbled slowly through the mixture.

The hydrogen tetracarbonylcobaltate(−I) formed was passed through a drying tube filled with calcium chloride, then precooled in a U-tube immersed in an ice bath. The gas mixture then was bubbled slowly through a mixture of 60 ml. of 1-butene (*ca.* 0.7 mole) and 10 ml. of pentane kept at −6 to −8°. The trap was fitted with a condenser kept at −30° to minimize loss of olefin. A 250-ml. solution of potassium tetracarbonylcobaltate(−I) containing approximately 0.12 mole of cobalt was used; thus, a large excess of olefin was present. This favors the formation of alkyl and acyl cobaltates(−I) and prevents the interaction of excess hydrogen tetracarbonylcobaltate(−I) with the above complexes to yield aldehydes.

After the gas had been bubbled through for 2–3 hr., the reddish solution was transferred rapidly to the autoclave under nitrogen, and the autoclave then was closed and heated between 120 and 130° for 3 hr. in order to decompose the carbonylcobaltates present.

The solution then was distilled, and the solvent and excess olefin were removed by aspirator vacuum. The high boiling product, 0.50 g., distilled below 40° (1 mm.).

The distillate was analyzed on a Perkin-Elmer 154-L gas chromatograph with a polyethyleneglycol distearate column. Peaks corresponding to *n*-valeraldehyde, 2-methylbutanal, 3,5-dimethyl-4-heptanone, 3-methyl-4-octanone, and 5-nonanone were observed.

An infrared spectrum of the distillate showed strong carbonyl absorptions around 5.8 μ.

Based on semiquantitative gas chromatographic estimates, the above compounds contribute roughly 80% of the product, the ketone to aldehyde ratio being about 9:1.

In another experiment, when no excess of olefin was present, this ratio was considerably smaller.

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# The Addition of Silicon Hydrides to Olefinic Double Bonds. IX. Addition of *sym*-Tetramethyldisiloxane to Hexene-1, -2, and -3

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*sym*-Tetramethyldisiloxane adds to either hexene-2 or hexene-3 in the presence of chloroplatinic acid to establish Si–C bonds with the silicon attached chiefly to the 1-position but also to the 2- and 3-positions of the hexyl group in the products. Hexene-1 formed the 1-hexyl derivative almost exclusively. During the reaction a hexene becomes a mixture of hexene isomers.

In the presence of platinum catalysts, chlorosilicon hydrides seem to add to acyclic olefins so as to form only primary alkylsilanes, even from olefins such as pentene-2,[1] heptene-3,[2] or 2-methylbutene-2.[3]

*sym*-Tetramethyldisiloxane behaves somewhat differently from the chlorosilanes in being able to form secondary alkylsilicon derivatives from an internal olefin. Heptene-3 apparently formed 1-, 3-, and 4-heptylsilicon compounds[2] by addition of *sym*-tetramethyldisiloxane.

During all such addition reactions isomerization of olefins may be observed.[3] Recent experiments with trichlorosilane-*d* ($Cl_3SiD$)[4] show that extensive exchange between Si–D and the C–H of the olefins accompany the isomerization. A plausible mechanism has been postulated[4] to rationalize these data. This mechanism seemed to indicate that a reaction that produced a 1-, a 3-, and a 4-heptylsilicon derivative from heptene-3 and tetramethyldisiloxane[2] must have produced also the 2-heptyl isomer. Heptene-3 also should have formed a mixture of the isomeric heptenes during the reaction. It was not observed to do so.[2]

To reconcile the earlier data[2] with more recent results,[4] essentially the same experiments were repeated using hexene-3, which was assumed to be chemically

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[2] J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958).

[3] J. C. Saam and J. L. Speier, *ibid.*, **83**, 1351 (1961).

[4] J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964).