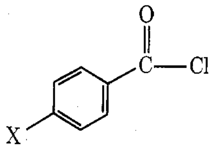
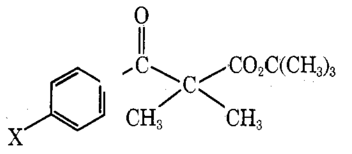
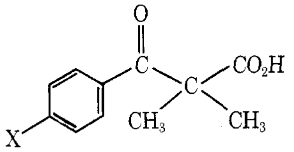


1a—e

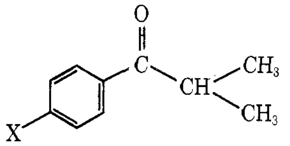


2a—e

a, X = H 55% **d**, X = Cl 68%
b, X = CH_3 68% **e**, X = NO_2 22%
c, X = OCH_3 80%



3a—e



4a—e

The nmr spectrum of **2a** in trifluoroacetic acid exhibited a *tert*-butyl resonance at δ 1.38 that disappeared after 45 sec with a simultaneous appearance of a new resonance (a singlet integrating for nine protons) at δ 1.60 that remained even after decarboxylation to **4a** was complete. The only reasonable assignment of the δ 1.60 resonance is to *tert*-butyl trifluoroacetate. Thus, isobutylene is not expelled from solution when esters **2** are dissolved in trifluoroacetic acid, but rather the elements of isobutylene are transferred from **2** to trifluoroacetic acid generating *tert*-butyl trifluoroacetate.[7] These observations clearly indicate that the original 15-min period used for the conversions of **2** to **3** was much longer than necessary.

This use of *tert*-butyl α-lithio esters offers great promise for the synthesis of a wide variety of substituted ketones, especially α-monoalkylated ketones that are difficult to prepare by other means. These aspects are presently under investigation.

The procedure for the synthesis of **2a** is representative.[8] To a solution of 20 mmol of *tert*-butyl α-lithioisobutyrate[9] dissolved in 25 ml of dry benzene at 0° was added a solution of 22 mmol of benzoyl chloride dissolved in 10 ml of dry benzene over 2 min. The cooling bath was removed and the reaction mixture allowed to come to room temperature. The reaction mixture was extracted with 10% potassium carbonate solution, washed with water and saturated brine, and filtered through anhydrous calcium sulfate. After the removal of solvent under reduced pressure, the yellow residue was chromatographed on silica gel with hexane to give **2a** as a colorless solid: mp 65.5–66.3°; ir (CCl_4) 1725, 1680, 1390, and 1385 cm^{-1}; nmr (CCl_4) δ 1.28 (s, 9), 1.47 (s, 6), 7.5–8.1 (m, 5).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available. The experimental procedures for the reactions described in this investigation will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-3455.

References and Notes

(1) Y. N. Kuo, J. A. Yahner, and C. Ainsworth, *J. Amer. Chem. Soc.*, **93**, 6321 (1971).
(2) M. W. Rathke and D. F. Sullivan, *Tetrahedron Lett.*, 1297 (1973).
(3) M. W. Rathke and J. Deitch, *Tetrahedron Lett.*, 2953 (1971), have used a similar method for the synthesis of ethyl β-keto esters, but these β-keto esters are not suitable for the preparation of β-keto acids, and difficulties are often encountered in converting them to ketones.
(4) L. Lochmann and D. Lim, *J. Organometal. Chem.*, **50**, 9 (1973), briefly mention the fact that *tert*-butyl α-lithioisobutyrate reacts with benzoyl chloride to give **2a**.
(5) No attempts have been made to optimize yields at this stage.
(6) All compounds were characterized by ir and nmr spectroscopy, and satisfactory combustion analyses were obtained for all new substances, except for the labile β-keto acids.
(7) G. A. Latremouille and A. M. Eastham, *Can. J. Chem.*, **45**, 11 (1967), have shown that *tert*-butyl trifluoroacetate is rapidly formed upon addition of isobutylene to cold (−40°) trifluoroacetic acid.
(8) In the case of **1e** an inverse addition of the *tert*-butyl α-lithioisobutyrate at −78° to *p*-nitrobenzoyl chloride was necessary in order to obtain **2e**.
(9) *tert*-Butyl α-lithioisobutyrate was prepared in the manner of *tert*-butyl α-lithioacetate; see M. W. Rathke and D. F. Sullivan, *J. Amer. Chem. Soc.*, **95**, 3050 (1973).

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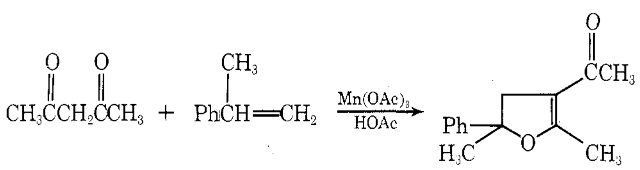
Oxidation by Metal Salts. XI. The Formation of Dihydrofurans

Summary: Dihydrofurans are formed in high yields by the reaction of readily enolizable ketones, such as β diketones and β-keto esters, with olefins in the presence of manganic acetate. The free-radical mechanism for their formation is presented and contrasted with the ionic mechanism observed in the case of lead tetraacetate, which leads to an isomeric product.

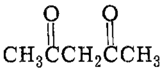
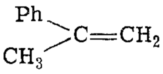
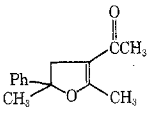
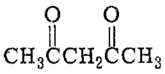
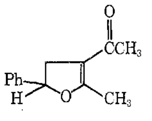
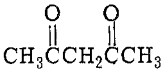
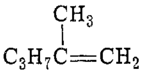
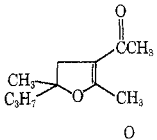
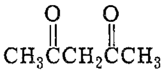
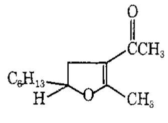
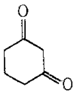
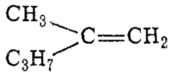
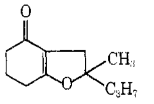
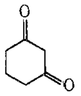
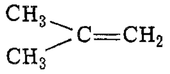
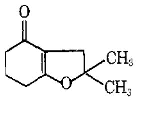
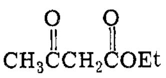
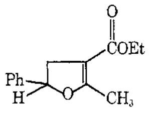
Sir: In an earlier communication[1] we described a novel free-radical addition reaction of enolizable ketones to olefins which took place in the presence of such oxidants as manganic acetate. The major products observed in these reactions were a saturated ketone, an unsaturated ketone, and a ketoacetate; the relative distribution of which depended on the reaction conditions and the nature of the reagents employed.

We now wish to report the facile formation of dihydrofurans in this reaction when highly enolizable ketones such as β diketones and β-keto esters are used as one of the reagents. Thus, the reaction of manganic acetate with acetylacetone and α-methylstyrene afforded the dihydrofuran[2] shown in quantitative yield, based on the manganic ion consumed. In a typical experiment, 0.25 mol of $Mn(OAc)_3\cdot 2H_2O$, prepared from potassium permanganate and manganous acetate,[3] was dissolved in 1 l. of glacial acetic acid at 45° under nitrogen. To this solution was added a mixture of 15.3 g of α-methylstyrene (0.13 mol) and 75 g of acetylacetone (0.75 mol). The reaction was over in 10 min as evidenced by the disappearance of the brown manganic color. The product dihydrofuran was isolated by extraction with ether followed by distillation. Examples of other dyhydrofurans synthesized *via* this method are shown in Table I.



The formation of these dihydrofurans can best be explained by our previously postulated mechanism[1,4] based on the selective generation of α-keto radicals from enolizable ketones and the selective oxidation of organic free radicals, the details of which are shown in Scheme I. The predominant formation of dihydrofurans from β-dicarbonyl compounds contrasts sharply with the low yield found in

Table I
Synthesis of Dihydrofurans

Ketone	Olefin	Dihydrofuran	Yield,[a] %
 $CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$			100
 $CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$	$PhCH{=}CH_2$		30
 $CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$	 $C_3H_7\overset{CH_3}{\overset{\|}{C}}{=}CH_2$		40
 $CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$	$C_6H_{13}CH{=}CH_2$		10 (33)[b]
			74
			>40
 $CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OEt$	$PhCH{=}CH_2$		57

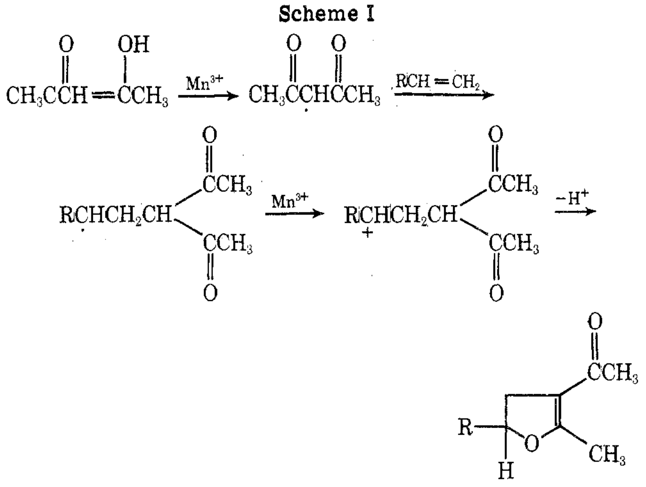
[a] Yields are based on Mn^{3+} consumed, assuming 2 equiv/mol of product. [b] In the presence of trifluoroacetic acid as cosolvent.

the case of simple ketones (2-methyl-5-phenyl-4,5-dihydrofuran was obtained as a very minor product in the reaction of acetone with styrene). This can be rationalized on the basis of the more rapid cyclization of the carbonium ion intermediate due to the greater enol content of these dicarbonyl compounds, as well as the greater stability of the resulting carbonyl-stabilized dihydrofuran products toward acid-catalyzed ring opening under reaction and work-up conditions.[5]

The dihydrofurans produced in the manganic acetate reaction of acetylacetone with terminal olefins have in all cases consisted of only one isomer, namely, the 5-substituted 2-methyl-3-acetyl-4,5-dihydrofuran. This stands in sharp contrast to the dihydrofuran reported in the thallic acetate reaction of acetylacetone with styrene,[6] where only the 4-substituted isomer was observed. The corresponding reaction of lead tetraacetate led to either one or both isomers, depending on the solvent employed.[7] At that time, two competing ionic mechanisms were proposed,[7] although the controlling factors for these two paths remained unexplained.

Our experience with manganic acetate now suggests that the 5 isomer is produced exclusively *via* a free-radical mechanism as depicted in Scheme I. The formation of the 4 isomer can then be rationalized by an ionic mechanism similar to that suggested,[6,7] in which a benzylic carbonium ion is produced by attack of the electrophilic metal acetate, which then, in turn, adds to the diketone.

Scheme I



The effect of solvent on the $Pb(OAc)_4$ reaction can be understood in terms of the well-established competition between ionic and free-radical pathways characteristic of lead tetraacetate,[8] both of which occur in the polar acetic acid solvent, whereas only the free-radical product is observed in benzene. This mechanistic explanation is consistent with the reported formation of the 5-substituted dihydrofuran in the electrochemical oxidative addition of sodium acetylacetonate to olefins,[9] which presumably is a free-radical reaction similar to that of manganic acetate.

The simple one-step synthesis of dihydrofurans presented in this communication represents one more example of syntheses based on the selective generation and oxidation of organic free radicals. Further examples of such syntheses will be presented in forthcoming publications.

Acknowledgment. The skillful technical assistance of George Stead is gratefully acknowledged.

References and Notes

(1) E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, **93**, 524 (1971).
(2) The dihydrofuran analyzed for $C_{14}H_{16}O_2$: mol wt (mass spectrum) 216; ir peaks at 5.96, 6.15, 6.24, 7.22, and 8.02 μ; nmr τ 8.35 (3 H, s), 7.85 (3 H, s), 7.7 (3 H, tr, J = 1.4 Hz), 6.9 (2 H, m), 2.7 (5 H, m).
(3) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **91**, 138 (1969).
(4) E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, **94**, 2888 (1972).
(5) L. H. Brannigan and D. S. Tarbell, *J. Org. Chem.*, **35**, 639 (1970).
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(8) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **90**, 2706 (1968); R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 771 (1967).
(9) H. Schafer and A. Alazrak, *Angew. Chem., Int. Ed. Engl.*, **7**, 474 (1968).

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Oxidation by Metal Salts. XII. A Novel One-Step Synthesis of 1,4 Diketones

Summary: A convenient one-step synthesis of 1,4 diketones by the reaction of enol esters with ketones in the presence of manganic acetate is presented.

Sir: As a continuation of our interest in the development of new synthetic methods based on the selective generation and oxidation of organic free radicals,[1] we wish to report a convenient one-step synthesis of 1,4 diketones from readily available starting materials. The development of new synthetic routes to 1,4 diketones has received considerable interest during the past few years, in view of their value as cyclopentenone precursors.[2]