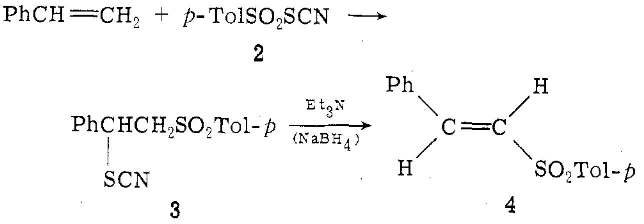
confirmed by the ir spectrum. Thus, all adducts in Table I showed a very strong, sharp band between 4.64 and 4.67 μ. Isothiocyanates are known to absorb at longer wavelength—4.67–5.26 μ—and these bands are usually broad.[10] We have been unable to detect any appreciable amount of isothiocyanate (by ir) in any of the crude reaction mixtures.[11]

That the reactions are homolytic in quality is supported by the nature of the adducts obtained which are analogous to those obtained in the known free-radical additions of sulfonyl iodides. Consistent also is the fact that large quantities of polystyrene were obtained in the reaction of methanesulfonyl thiocyanate with styrene. The biting odor of sulfur dioxide was noted during the reactions in which alkanesulfonyl thiocyanates were employed; this observation is consistent with the intermediacy of $RSO_2\cdot$, which decomposes to $R\cdot$ and SO_2.

The yields listed in Table I have not been optimized though it has been found that these additions require a large excess of hydrocarbon for best results. Thus, in reaction 2, as the molar ratio of cyclohexene was increased in the manner 1:1, 2:1, 4:1, and 10:1, the corresponding yields of isolated product were 15, 38, 53, and 84%. The yields given in Table I are the result of hydrocarbon excesses ranging from 2:1 to 10:1.

Careful monitoring of several of the reactions (1–4, 9) by both tlc and glpc methods has revealed, in addition to starting materials and very slow moving components (most certainly polymeric in nature) no more than 10% minor products with R_f values and retention times comparable with those of the isolated adducts.



That structure 3 correctly represents the adduct obtained in the p-toluenesulfonyl thiocyanate addition to styrene was confirmed by its further, facile conversion to 4 (93%). Based on the known trans additions of sulfonyl iodides, it seems reasonable to assign structures resulting from trans addition of the sulfonyl and thiocyanato moieties in reactions 2–8; however, this matter is currently under investigation.

The spectral data of the adducts from reactions 9 and 10 confirm that addition has occurred to the less substituted double bond. The nmr spectrum of the adduct from reaction 10 shows three unequal methyl groups as singlets, in addition to a methylene group (singlet). With 9, one of the methyl groups is replaced by a p-tolyl function. That the thiocyanato group was attached to the terminal carbon was determined by the interesting borohydride conversion of this latter adduct to 2-(p-toluenesulfonyl)-3-methylbut-1-ene in 57% yield. Similar borohydride treatment of 3 provided 4 in 88% yield.

Though the chemistry of these 1:1 adduts may, in some respects, resemble that found when sulfonyl iodides are employed, the presence of the thiocyanato moiety in the current compounds provides an unusually reactive functionality which should be subject to the known transformation of thiocyanates,[6] thereby providing access to numerous unique β-substituted sulfones.

Acknowledgment. Thanks are expressed to Dr. R. T. Blickenstaff for his encouragement and suggestions and to G. Wagoner for technical assistance.

Supplementary Material Available. A full experimental section describing the synthesis of all adducts in Table I, as well as the preparation of **4**, **6**, and p-toluenesulfonyl thiocyanate will appear following these pages in the microfilm edition of this volume of the journal. Additionally, full nmr, ir, and analytical data are tabulated. 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-74-3454.

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(2) W. E. Truce and G. C. Wolf, *J. Org. Chem.*, **36**, 1727 (1971).
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(4) (a) A. M. van Leusen, A. J. W. Iedema, and J. Strating, *Chem. Commun.*, 440 (1968); (b) J. M. Cox and R. Ghosh, *Tetrahedron Lett.*, 3351 (1969); (c) R. G. Pews and F. P. Corson, *Chem. Commun.*, 1187 (1969).
(5) R. G. Pews and T. E. Evans, *Chem. Commun.*, 1397 (1971), and references cited therein.
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(7) Unknown at the outset of this work was a patent briefly describing the preparation of five arylsulfonyl thiocyanates [J. Goerdeler and P. Rosenthal, German Patent 1,219,021 (1966); *Chem. Abstr.*, **66**, 2371 (1967)]; further details concerning the properties and reactions of these materials have not been forthcoming.
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(9) (a) R. G. R. Bacon and R. G. Guy, *J. Chem. Soc. (London)*, 2428 (1961); (b) R. G. R. Bacon, R. G. Guy, and R. S. Irwin, *ibid.*, 2436 (1961).
(10) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 117.
(11) The possibility of obtaining isothiocyanates was validly raised by one of the reviewers; we have found, and intend to report in detail later, that indeed some of our adducts may be readily isomerized to the corresponding isothiocyanates.

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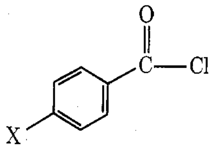
Condensation of *tert*-Butyl α-Lithioisobutyrate with Acid Chlorides. A Synthesis for β-Keto Acids and Ketones

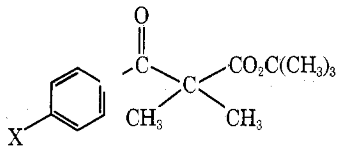
Summary: The acylation of *tert*-butyl α-lithioisobutyrate with benzoyl chlorides gives the corresponding β-keto esters in good yield, and subsequent treatment of these esters with trifluoroacetic acid either at room temperature or at reflux affords β-keto acids or isobutyrophenones, respectively.

Sir: Recently dianions of carboxylic acids[1] and O-silyl ketene acetals[2] have been used to prepare β-keto acids and β-keto esters, respectively. However, the former method does not work well for the preparation of α-benzoyl carboxylic acids and the latter method is inapplicable to the synthesis of α,α-disubstituted β-keto esters. Herein we report a new procedure[3] for the facile synthesis of both of these classes of compounds and for their conversion into the corresponding ketones.

Treatment of *tert*-butyl α-lithioisobutyrate with benzoyl chlorides (**1**) gave the *tert*-butyl α-benzoylisobutyrates[4] (**2**) in fair to good yields.[5] The *tert*-butyl esters **2** upon treatment with trifluoroacetic acid for 15 min at room temperature afforded the β-keto acids[6] **3** in quantitative yield. The corresponding ketones **4** can be readily prepared, essentially quantitatively, by heating solutions of **2** in trifluoroacetic acid under reflux for 1 hr.

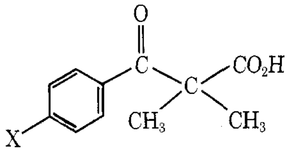


1a—e

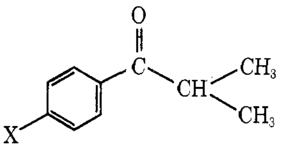


2a—e

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.

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(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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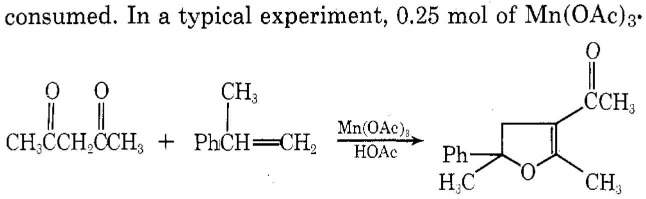
Oxidation by Metal Salts. XI.
The Formation of Dihydrofurans

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