

This addition required 30 min. An additional 30 min. was allowed for complete reduction. The nickel catalyst was removed by filtration through a Büchner funnel and washed thoroughly with ethanol. The aqueous ethanolic filtrate was saturated with sodium chloride and the oil which separated was extracted with ether. Distillation of the ether

extract after drying it with magnesium sulfate yielded 18 g. (75%) of a colorless oil, b.p. 104–105° (17 mm.), n_D^{20} 1.5269. Reported⁸ for methylphenylcarbinol: b.p. 93° (16 mm.), n_D^{20} 1.5251.

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The Thermal Decarboxylation of β -Alkoxyacrylic Acids. A New Synthesis of Isopropenyl Ethers

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A number of alkyl isopropenyl ethers have been obtained in good yield and in high purity by thermal decarboxylation of the corresponding β -alkoxyacrylic acids. It appears that the reaction may be useful as a preparative route to compounds of the type $R_1COR_2=CHR_3$, $R_1CSR_2=CHR_3$, and $R_1CNR_2R_3=CHR_4$; possible limitations of the procedure are outlined. *p*-Methoxybenzyl isopropenyl ether was found to rearrange to 4-*p*-methoxyphenyl-2-butanone.

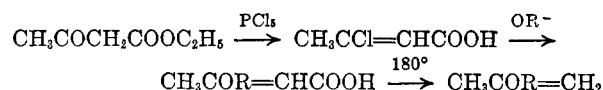
The literature contains a number of scattered observations that substituted β -alkoxyacrylic acids are readily decarboxylated. In 1896, Autenrieth reported that β -benzoxycrotonic acid upon melting decomposed to form carbon dioxide and benzyl isopropenyl ether; the corresponding thioether was obtained in the same way.¹ Phenyl isopropenyl ether was similarly obtained by Ruhemann and Wragg.² A different course appeared to be followed by β -methoxymethoxycrotonic acid, which upon being heated yielded $CH_3(CH_2OCH_2O)C=CHCOOCH_2OCH_3$ rather than the acetal $CH_3(CH_2OCH_2O)C=CH_2$.³

Although the simple decarboxylation affords a potentially useful method of preparing substituted vinyl ethers, sulfides, and amines, it appears to have been neglected since the early work, perhaps because other methods are often applicable. The alternative procedures however involve a number of drawbacks. Reppe's method of adding alcohols to acetylenic linkages requires high pressures; dehydrohalogenation of saturated β -chloro ethers^{4,5} requires the use of solid sodium hydroxide and high temperatures, as well as an organic reactant often not easily available; catalytic cleavage of acetals often leads to extensive side reactions⁶ and a recent procedure⁷ involving the use of vinylmercury compounds is useful principally for thioethers and aryl vinyl ethers.

The precursor acids for the decarboxylation reaction are readily prepared from β -keto esters, and in view of the current lively interest in the reactions

of vinyl ethers,^{8a-e} it appeared desirable to learn the scope and principal limitations of the reaction. To date, it has been found that the decarboxylation of β -alkoxyacrylic acids proceeds easily and in high yields to give the pure vinyl ethers for most of the simple alkoxy groups, but side reactions become important when electron donating groups render the ether linkage sensitive to even weak acids.

The general approach is as follows:



There appear to be no limitations in the first step, though the yield varies widely. For instance, if the starting material is ethyl acetoacetate, about 30–40% β -chlorocrotonic acid is obtained (after hydrolysis of the acid chloride initially formed) whereas with ethyl benzoylacetate the yield is nearly quantitative. Isolation of the product is mildly complicated by the fact that both *cis* and *trans* isomers may result; however, they need not be separated since both lead to the same product in the following step.

Jones⁹ has observed that nucleophilic displacement of vinylic halide is greatly facilitated by the presence of a β -carbonyl group. Likewise we found that β -alkoxy acids are readily produced when a solution or suspension of sodium β -chlorocrotonate in an alcohol containing an excess of alkoxide ion is refluxed. The yields were generally fair (50–75%); in a few experiments premature decarboxylation lowered the yield. Since the acid chlorides

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(3) J. L. Simonsen and L. Storey, *ibid.*, **95**, 2106 (1909).

(4) For some examples, see V. L. Tweedie and B. G. Barron, *J. Org. Chem.*, **25**, 2023 (1960).

(5) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1910 (1938).

(6) W. J. DeJarlais, J. L. O'Donnell, and H. M. Teeter, *J. Am. Oil Chemists' Soc.*, **38**, no. 5, 241 (1961).

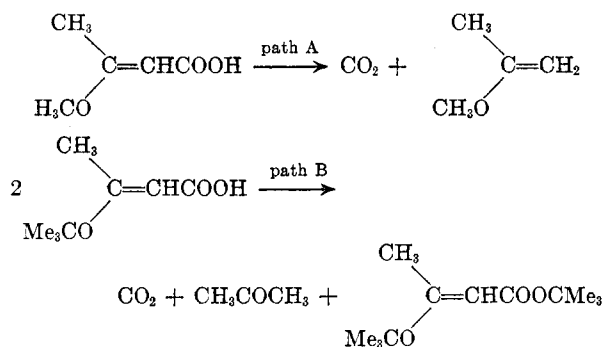
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initially formed in the first step can be readily converted to esters, and since the vinylic halide in these esters is equally easily displaced by alkoxide ion,⁹ better yields may be obtained *via* this route, which has not yet been explored. β -*t*-Butoxycrotonic acid was obtained by the base-catalyzed addition of *t*-butyl alcohol to tetrolic acid¹⁰ and β -methoxymethoxycrotonic acid from the reaction of chloromethyl methyl ether with ethyl acetoacetate,³ and unusual reaction in which *O*-alkylation is presumably the result of the highly polar nature of the carbon chlorine bond in that halide.¹¹

The decarboxylation proceeds rapidly and completely simply by maintaining the acid at 180°; the ether distills in analytical purity. One side reaction is observed if the ether linkage may be expected to be sensitive to acids; *i.e.*, if the alkyl group bound to the oxygen atom can readily accommodate a positive charge. The primary products then are carbon dioxide, acetone, and an ester of the original acid. An example is shown below.



The fate of a number of β -alkoxycrotonic acids when heated to 180° is shown in Table I.

TABLE I
MODE OF REACTION OF β -ALKOXYCROTONIC ACIDS UPON HEATING TO 180°

Alkoxy group	Path A,	Path B,
	%	%
—OCH ₃	99	0
—OC ₂ H ₅	100	0
—O- <i>n</i> -C ₃ H ₇	92	0
—O- <i>i</i> -C ₃ H ₇	99	0
—OCH ₂ CH=CH ₂	100	0
—O- <i>n</i> -C ₈ H ₁₇	100	0
—O-cyclo-C ₆ H ₁₁	100	0
—O- <i>t</i> -C ₄ H ₉	60	40
—O- <i>p</i> -CH ₂ C ₆ H ₄ OCH ₃	42	58
—OCH ₂ OCH ₃	18	82

The numbers in Table I were obtained by isolation of the products as well as by measurement of the pressure of the carbon dioxide, that of the acetone and that of the volatile ether evolved by a small known amount of acid by the use of a vacuum line technique described in the Experimental. In some experiments, the products reacted further

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(11) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Ifland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

to give secondary products. Allyl isopropenyl ether was completely converted into 5-hexen-2-one, as should be expected from a Claisen rearrangement. *t*-Butyl isopropenyl ether eliminated isobutylene, the other fragment being acetone; the ester obtained in the decarboxylation reaction likewise gave isobutylene and *t*-butyl acetoacetate. Formaldehyde methyl isopropenyl acetal could be isolated in crude form; it slowly decomposed into acetone and an unidentified polymeric material. *p*-Methoxybenzyl isopropenyl ether was also obtained in crude form; it polymerized in attempts to purify it by elution chromatography, while in a gas chromatographic column at 235° it isomerized to 4-*p*-methoxyphenyl-2-butanone.

While the present work was primarily concerned with one variable (the ether linkage), it is obvious that the reaction is not restricted to the formation of isopropenyl ethers. Since β -keto esters are generally readily available and since these compounds can be alkylated before reaction with phosphorus pentachloride, a wide variety of alkyl vinyl ethers should be available by this path.¹² Its resemblance to the preparation of ketones and substituted acetic acids *via* β -keto esters is obvious; in fact, the first two steps in the procedure amount of *O*-alkylation of the β -keto ester. The main differences are the cleanliness of decarboxylation in this work and the somewhat greater stability of β -alkoxycrotonic acids as compared to β -alkylacetoacetic acids, so that isolation and purification of these precursors is possible when desired. Furthermore, the greater nucleophilicity of mercaptide ions should allow preparation of alkyl isopropenyl sulfides by this route also; one example of this has already been noted. It may well be that enamines can be obtained in the same way.

The several β -alkoxycrotonic acids were obtained in but one of the two possible geometric forms. Present evidence is insufficient to prove whether it is *cis* or *trans*. Slight evidence for the latter is the ultraviolet absorption at 235 m μ for β -methoxycrotonic acid in 2,2,4-trimethylpentane obeying Beer's law up to a concentration of 3×10^{-5} but not higher. *o*-Methoxybenzoic acid, which has methoxy and carboxyl groups in *cis* positions, behaves in this manner.¹³

(12) It is not clear however, that the ease of nucleophilic displacement of vinylic halide by alkoxide ion is independent of the presence of a H-atom on the adjacent carbon atom. Jones (see ref. 9) has found that ethoxide ion reacts with ethyl β -chloro- α -methylcrotonate roughly 100 times more slowly than with ethyl β -chlorocrotonate, but found evidence to support the conclusion that addition of ethoxide precedes elimination of the chloride ion, and that the α -proton is not involved in the process; on the other hand, there are examples in which elimination of HX precedes addition of the alcohol. This mechanism, which involves an acetylene as an intermediate is obviously not possible in the absence of an α -proton [see *e.g.* G. Huett and S. I. Miller, *J. Am. Chem. Soc.*, **83**, 408 (1961)]. In some preliminary experiments it was found that ethyl 2-chloro-1-cyclopentene-1-carboxylate is not attacked by alkoxide ion under even rather drastic conditions.

(13) W. F. Forbes, A. R. Knight, and D. L. Coffen, *Can. J. Chem.*, **38**, 728 (1960).

The vinyl ethers obtained in this work had a split band at 1625 cm.^{-1} , which supports the suggestion^{8e} that vinyl ethers may exist in two conformations. Further evidence comes from the observation¹⁴ that the intensity ratio of these two bands is dependent on the temperature.

A further point of interest is provided by *p*-methoxybenzyl isopropenyl ether. It is well known⁵ that vinyl allyl ethers undergo Claisen rearrangement to the corresponding 5-pentenals; the formation of 5-hexen-2-one mentioned earlier is an example. A similar reaction is the formation of *o*-allylphenols from allyl phenyl ethers, where the vinylic double bond is part of a benzene ring. There appears to be no knowledge of whether rearrangement takes place when the allylic double bond is part of a benzene ring¹⁵; *i.e.* formation of *o*-tolylacetaldehydes from benzyl vinyl ethers. Two members of this class of compounds are known; benzyl vinyl ether itself¹⁶ and benzyl isopropenyl ether,¹ both of which survive vacuum distillation. In an attempt to purify *p*-methoxybenzyl isopropenyl ether by gas chromatography at 235° , isomerization did take place, but instead of (2-methyl-5-methoxyphenyl)acetone the rearranged product turned out to be 4-*p*-methoxyphenyl-2-butanone, which may be considered the product of a Claisen rearrangement without inversion of the "allylic" group.

Experimental

Materials.—The β -alkoxy acids listed below were prepared by refluxing solutions or suspensions of 0.1 mole of sodium β -chlorocrotonate (either *cis* or *trans*) with a twofold excess of the sodium alkoxide (1–2 *N*) dissolved in the appropriate alcohols, all of which were carefully dried. Refluxing usually was maintained for 3 hr., longer for alcohols boiling below 100° . An aqueous solution of the product salt was obtained by flash evaporation (when feasible), addition of water, and extraction with ether. The aqueous solution was acidified with dilute hydrochloric acid to pH of 3.5. The precipitate was washed and dried *in vacuo* before recrystallization from hexane or methanol; incomplete removal of water and mineral acid in some instances resulted in decomposition of the product to carbon dioxide, acetone, and the original alcohol. β -Methoxycrotonic acid, m.p. $131\text{--}132^\circ$ (130°),¹⁰ neut. equiv. 115.5 (116.1); β -ethoxycrotonic acid, m.p. $139\text{--}140^\circ$ (140°),¹⁰ neut. equiv. 129.8 (130.1); β -*i*-propoxycrotonic acid, m.p. $104\text{--}105^\circ$ (106°),¹⁰ neut. equiv. 146.9 (144.2); β -*n*-propoxycrotonic acid, m.p. $102\text{--}103^\circ$, neut. equiv. 144.8 (144.2). *Anal.* Calcd. for $\text{C}_7\text{H}_{12}\text{O}_3$: C, 58.31; H, 8.39. Found: C, 58.14; H, 8.34. β -*p*-Anisoxycrotonic acid, m.p. $150\text{--}151^\circ$, d, neut. equiv. 225 (222). *Anal.* Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_4$: C, 64.86; H, 6.31. Found: C, 64.73; H, 6.56. β -Alloxycrotonic acid, m.p. $79\text{--}81^\circ$, neut. equiv. 143.9 (142.2). *Anal.* Calcd. for $\text{C}_7\text{H}_{10}\text{O}_3$: 59.14; H, 7.09. Found: C, 58.86; H, 7.18. β -*n*-Pentoxycrotonic acid, m.p. $70\text{--}72^\circ$, neut. equiv. 171.9 (172.2). *Anal.* Calcd. for $\text{C}_9\text{H}_{16}\text{O}_3$: C, 62.76; H, 9.37. Found: C, 62.76; H, 9.32. β -Cyclohexoxycrotonic acid, m.p. $97\text{--}99^\circ$, neut. equiv. 183.5 (184.2). *Anal.* Calcd. for $\text{C}_{10}\text{H}_{16}\text{O}_3$: C, 65.19; H, 8.76. Found: C, 65.27; H, 8.89.

(14) P. P. Shorygin, T. H. Shkurina, M. F. Shostakovskii, and E. P. Gracheva, *Bull. Acad. Sci. USSR* (transl.), 935 (1961).

(15) D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1945, p. 1.

(16) *Cf. Chem. Abstr.*, **48**, 633f (1954).

β -*t*-Butoxycrotonic acid was obtained by the base-catalyzed addition of *t*-butyl alcohol to tetrolic acid; m.p. $126\text{--}127^\circ$ (127°).¹⁰ β -Methoxymethoxycrotonic acid was prepared by the alkylation of ethyl sodioacetoacetate by chloromethyl methyl ether in diglyme solution, m.p. 105° (105°),³ neut. equiv. 147.0 (146.1). The yields in every case fell between 50 and 75% with the exception of β -alloxycrotonic acid, of which only 10% was obtained.

Decarboxylation Procedures.—Decarboxylations were carried out on a 0.05 *M* scale in a side-arm flask provided with a nitrogen inlet tube; the side arm was connected to a U-trap cooled in ice, or in a Dry Ice-acetone slush when the more volatile ethers were generated. The contents of the flask were cautiously heated (with a free flame); generally there was very little or no residue left when carbon dioxide evolution ended. The product was usually obtained in quantitative yield and in analytical purity (procedure I). Alternatively, 5–15 mmoles of the acid were sealed into an evacuated 500-ml. bulb provided with a break-off seal. The bulb was stored in an oven at 180° for 3 hr.; after cooling, the volatile part of the contents was expanded into a calibrated vacuum line which allowed its separation by distillation to traps held at various low temperatures. This method (procedure II) allowed identification and estimation of carbon dioxide by means of its infrared spectrum,¹⁷ molecular weight (generally in the range of 43–45), and its pressure. The amount of carbon dioxide evolved was one indication of what fraction of the alkoxy acid decomposed to form the corresponding ether (one mole of carbon dioxide per mole of acid decomposed) and what fraction decomposed to form the ester (one-half mole of carbon dioxide per mole of acid); another indication was the amount of acetone formed. Acetone (one-half mole per mole of acid decomposing to the ester) was identified by its infrared spectrum, molecular weight (in the range of 57–59), and in some cases by its 2,4-dinitrophenylhydrazone derivative; the yield was determined from its pressure. The product ethers were identified by means of their infrared spectra (strong bands at 1090 and 1290 cm.^{-1} and a split $\text{C}=\text{C}$ stretching band at 1625 cm.^{-1} , refractive index, molecular weight (within a few per cent of theoretical values) and $\text{C}-\text{H}$ analysis; yields were determined from the pressures. The residues were collected and distributed between ether and water; the aqueous part was titrated to detect undecomposed acid (usually a few per cent or less) and the ether solution was treated to yield the ester as shown below. Yields of ether products by this procedure were always nearly quantitative (after correction for unchanged acid), except of course when ester formation also took place, and again in analytical purity.

These alkyl isopropenyl ethers were isolated: alkyl = methyl, ethyl, propyl, isopropyl, and cyclohexyl. All are known compounds^{18–20}; all were analyzed and of analytical purity as collected; *e.g.* for the methyl ether; C, 66.61; H, 11.06 (calcd., C, 66.63; H, 11.18). The boiling point and index of refraction data were in close agreement with literature values.

β -Alloxycrotonic acid upon decarboxylation yielded only carbon dioxide and 5-hexen-2-one whose infrared spectrum was found to be identical with that of the known compound, b.p. 131° (129°),⁵ n_D^{20} 1.4176 (1.4174),²¹ semicarbazone, m.p. $96\text{--}98^\circ$ ($99\text{--}100^\circ$).²² β -Methoxymethoxycrotonic acid (6.54 mmole) yielded 3.84 mmoles of carbon dioxide and 3.2 mmoles of acetone contaminated by a small amount of

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a gas whose infrared spectrum was that expected for formaldehyde methyl isopropenyl acetal; this material could be concentrated by gas chromatography but not purified for analysis, as it decomposed slowly to acetone and a polymer not further identified. The residue was purified by a short path distillation; n_D^{25} 1.4540. The product had the correct analysis for methoxymethyl (β -methoxymethoxy) crotonate.

Anal. Calcd. for $C_9H_{14}O_3$: C, 50.52; H, 7.42. Found: C, 51.12; H, 7.52.

A chemical structure proof for this material has been given by Simonsen³; no physical properties are available for comparison. β -(*p*-Methoxybenzyloxy)crotonic acid (15 mmoles) similarly yielded 10.6 mmoles of carbon dioxide, 4.0 mmoles of acetone, and a compound whose infrared spectrum was characteristic of isopropenyl ethers. Attempts to purify this material by elution chromatography on alumina resulted in its polymerization; an attempt to purify it by gas chromatography (235°, Silicone 90 column) resulted in the isolation of 4-*p*-methoxyphenyl-2-butanone, m.p. 9.5–10° (9.7–9.8°).²³

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.11; H, 7.92. Found: C, 73.88; H, 8.09.

Semicarbazone, m.p. 167–168° (169–170°).²⁴

The residue was chromatographed on an alumina column eluted by hexane–benzene mixtures. This resulted in a

yellow solid, white after treatment with activated charcoal and recrystallization from 25% benzene–75% hexane, m.p. 74–76°.

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.37; H, 6.62.

Prolonged base-catalyzed hydrolysis of this ester (which turned out to be very resistant to such treatment) resulted in the formation of the parent acid (m.p. undepressed upon admixture) and *p*-methoxybenzyl alcohol, recognized by its infrared spectrum. β -*t*-Butoxycrotonic acid (4.36 mmoles) yielded 3.5 mmoles of carbon dioxide, 3.5 mmoles of acetone, 2.6 mmoles of isobutylene, recognized by its infrared spectrum,²⁵ and a residue that after a short path distillation yielded a compound whose infrared spectrum (two carbonyl peaks) and gas chromatographic behavior (two widely separated but unresolved peaks) are characteristic of β -keto esters; n_D^{25} 1.4178 (1.4178).²⁶

Anal. Calcd. for $C_9H_{14}O_3$ (*t*-butyl acetoacetoacetate): C, 60.74; H, 8.92. Found: C, 61.35; H, 8.98.

Acknowledgment.—The authors gratefully acknowledge financial support by the Research Corporation (Frederick Gardner Cottrell Grant No. PN-2099).

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Substituted 1,10-Phenanthrolines. XIV. Hydroxy and Methoxy Derivatives¹

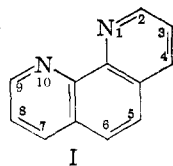
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With the object of preparing new chelates of iron(II) and copper(I) the following 1,10-phenanthrolines have been synthesized: 2- and 5-hydroxy-; 4-hydroxy-5-methoxy- and 4,5-dihydroxy-; 4,7-dimethoxy-, -diphenoxy-, and -diamino-; 5,6-dimethoxy- and dihydroxy-; 3-carboxy-5,6-dimethoxy-4-hydroxy- and 3-carboxy-4,5,6-trihydroxy-; 4-hydroxy-5-methoxy-2-methyl- and 4,5-dihydroxy-2-methyl-; 2,4-dihydroxy-5-methoxy- and 2,4-dihydroxy-

Substitution of alkyl and aryl groups in the nucleus of 1,10-phenanthroline (I) has in general



been found to increase its chelating power for iron (II) and copper (I). These complex cations are for the most part stable when the pH of the solution is relatively low. The corresponding chelates of 4,7-dihydroxy-1,10-phenanthroline,³ however, have been found to be stable in solutions of higher pH, and even in concentrated alkaline solution if excess ligand is provided. The present investigation seeks

to furnish more of these hydroxyphenanthrolines for study, as well as certain methoxy derivatives, this type of substitution having previously been untested.

2-Hydroxy-1,10-phenanthroline was obtained by hydrolysis of 2-methoxy-1,10-phenanthroline by hydrogen iodide. The latter compound was prepared by a Skraup reaction (Yale modification⁴) on 8-amino-2-methoxyquinoline,⁵ rather than from 2-chloro-1,10-phenanthroline as previously reported.⁶

5-Hydroxy-1,10-phenanthroline resulted from the hydrolysis of the corresponding methoxy derivative, obtained by us from 8-amino-6-methoxyquinoline⁷ in a Skraup reaction rather than from 5-chloro-1,10-phenanthroline⁸ as previously reported. The decarboxylation of 4-hydroxy-5-methoxy-1,10-phenanthroline-3-carboxylic acid⁸

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