

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MIAMI]

## Studies of Thermal Decarboxylation of Iron Carboxylates. I. Preparation of Symmetrical Aliphatic Ketones<sup>1,2</sup>

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The thermal decarboxylation of iron carboxylates has been demonstrated to be an excellent method for the preparation of symmetrical, straight chain, aliphatic ketones. Some anomalous results are also reported.

The intermolecular decarboxylation of alkaline earth salts of carboxylic acids is frequently cited as a general method useful for the preparation of carbonyl compounds. A recently published critique<sup>3</sup> of this reaction presents evidence that yields are

low and the expected carbonyl compounds are mixed with a variety of homologous compounds. Easterfield and Taylor<sup>4</sup> reported the syntheses of symmetrical ketones in yields of 60–80% by the reaction of straight chain fatty acids with iron filings, followed by distillation. They worked successfully with carboxylic acids of eighteen to thirty carbon atoms, but reported negative results

(1) Abstracted in part from the M.S. thesis of Robert Davis, University of Miami (1961).

(2) Presented before the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept. 3–8, 1961.

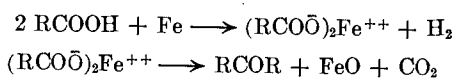
(3) H. Schultz and J. Sickels, *J. Chem. Educ.*, **38**, 300 (1961).

(4) T. Easterfield and C. Taylor, *J. Chem. Soc.*, **99**, 2298 (1911).

from such simple acids as ethanoic acid, butanoic acid, and phenylethanoic acid. Ruzicka *et al.*,<sup>5</sup> later reported the preparation of 1,20-henicosadiene-11-one in good yield from 10-undecenoic acid.

The purpose of this paper is to report the successful syntheses of symmetrical ketones from the iron salts of the lower molecular weight fatty acids, as well as a study of the influence of certain substituents upon the reaction.

In essence, it was demonstrated that when fatty acids were refluxed with iron powder, hydrogen was evolved and the iron(II) carboxylates formed. When heated, the iron(II) carboxylates decomposed to yield symmetrical ketones, ferrous oxide, and carbon dioxide.

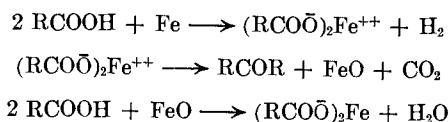


Salt formation occurred very rapidly with ethanoic and propanoic acids; butanoic acid and higher members of the series reacted at lower but relatively constant rates with iron powder, evolution of hydrogen beginning at 80–140°.

The iron carboxylates were deduced to be ferrous in nature. This deduction was based upon a number of observations. It was noted that as salt formation progressed, the material assumed the light green color characteristic of iron compounds in which iron exists in the iron(II) oxidation state. If the cooled salts were exposed to air, the surface would immediately turn dark brown; however, cool iron carboxylates covered with dry nitrogen exhibited no change in the light green color. Also, the crude distillates from iron salts of butanoic through heptanoic acids all had light green colors while protected from air; all gave positive tests for iron(II) ion (precipitation of Prussian blue on addition of potassium ferricyanide solution); all turned from light green to light brown on contact with air, and on redistillation, the crude yields left a trace of brown ferric oxide. (Only the acids cited above gave iron salts of a sufficiently high vapor pressure to distil in detectable quantities into the crude yield). Hexanoic acid gave a yield of 70% of ketone with little tar formation when treated with one equivalent of iron. The dry, nonmagnetic, black powder remaining as a residue after destructive distillation of the iron(II) hexanoate was protected from air with dry nitrogen; this residue of iron(II) oxide was treated with an equivalent of hexanoic acid, refluxed, and again destructively distilled to give 63% of pure ketone. The black residue from the second reaction was also without tar and was not magnetic. The oxide was scraped from the flask, finely powdered, and dried in air several days. At this point the black iron oxide residue was strongly magnetic. It was again treated with a third portion of an equivalent of hexanoic

acid to yield only 2% of ketone. Commercial iron-(II,III) oxide (magnetic iron oxide) gave only 4% of ketone when treated with hexanoic acid. Commercial iron(III) oxide gave no ketone from hexanoic acid.

Decomposition of the iron(II) carboxylates occurred in most instances at 250–300°; iron(II) ethanoate and propanoate were, however, amazingly stable up to 400–500°. To eliminate the possibility of loss of volatile carbonyl products during decarboxylation of iron(II) ethanoate and iron(II) propanoate, the evolved vapors were condensed in an ice water condenser and the gases were bubbled through a cold alcohol trap. The alcohol from this trap gave no precipitate with 2,4-dinitrophenylhydrazine reagent. The relatively poor yields of propanone and 3-pentanone cited in Table I may be explained by the fact that at the very high temperature required for the decomposition of iron(II) ethanoate and iron(II) propanoate, uncontrolled scission of other bonds of the molecule occurred. Reasonable explanation for the great stability of these salts as compared with those of longer chain acids is difficult. It is possible that longer chain acid moieties have a greater shielding effect toward iron(II) cation than do the smaller ethanoate and propanoate units, thus decreasing coulombic attraction between iron(II) cation and organic anion and resulting in a less ionic crystal lattice. This hypothesis was supported by two further observations: that the melting points of the iron salts decreased with increasing carbon chain length, and that the vapor pressures of the salts of acids of four carbon atoms or more were higher than either the iron(II) ethanoate or iron(II) propanoate. The vapor pressures of the iron salts of acids of four or five carbon atoms were found to be greater than all others of the series. Indeed, the iron salts of 2-methylpropanoic, 2-methylbutanoic, and 2,2-dimethylpropanoic acids sublimed extensively during attempts at destructive distillation. Those acids whose reflux temperatures were above the decomposition temperatures of the iron salts formed produced salts which decomposed during initial refluxing. The ferrous oxide thus formed reacted with more acid to give more iron(II) carboxylate for decomposition.



Although all data reported in Table I were obtained by reaction of an equivalent of acid with an equivalent plus 10% of iron, the potential utility of the use of a catalytic amount of iron in certain cases was demonstrated. Butanoic acid, b.p. 162–164°, gave a 70% yield of ketone from an equivalent of iron, and only a 35% yield of ketone from one-half of an equivalent of iron powder; undecanoic

(5) L. Ruzicka, M. Stoll, W. Sherrer, H. Schinz, and C. Seidel, *Helv. Chim. Acta*, 15, 1465 (1932).

TABLE I  
DECARBOXYLATION PRODUCTS FROM IRON(II)  
CARBOXYLATES

Acid	Products	%
Ethanoic	Propanone	25
Phenylethanoic	1,3-Diphenylpropanone	71
Methoxyethanoic	Methanol	1
Phenoxyethanoic	Phenol	60
Propanoic	3-Pentanone	48
2-Methylpropanoic	2,4-Dimethylpentanone-3	53
2,2-Dimethylpropanoic	None	—
3-Phenylpropanoic	1,5-Diphenylpentanone-3	43
Butanoic	4-Heptanone	70
<i>trans</i> -2-Butenoic	None	—
2-Methylbutanoic	None	—
3-Methylbutanoic	2,6-Dimethylheptanone-4	46
4-Phenylbutanoic	1,7-Diphenylheptanone-4	35
Pentanoic	5-Nonanone	69
Hexanoic	6-Undecanoic	70
Heptanoic	7-Tridecanone	74
Octanoic	8-Pentadecanone	80
Nonanoic	9-Heptadecanone	91
Decanoic	10-Nonadecanone	96
Undecanoic	11-Henicosanone	91

acid, b.p. ca. 280°, on the other hand, gave 91% of ketone with either set of reaction conditions!

The mechanism of ketonic, thermal decarboxylation reactions is still not completely elaborated; however, three significant and consistent papers on this mechanism have been published.<sup>6-8</sup> These papers propose an aldol-type condensation mechanism which requires that a carboxylic acid possess at least one alpha hydrogen atom in order to undergo the ketonic decarboxylation reaction. The completely negative results observed from the attempted ketonic decarboxylation of 2,2-dimethylpropanoic acid are consistent with the current views on the mechanism of the ketonic decarboxylation reaction.

The drop in yield observed as a phenyl group is substituted onto the terminal carbon atom of ethanoic, propanoic, and butanoic acids respectively, may indicate increasing intramolecular interaction between the unsaturation pi electrons of the benzene ring and iron of the carboxylate salt. As the number of atoms between benzene ring and carboxylate group increases from one to three carbon atoms, the benzene ring may be shown to have the possibility of lying closer to the carboxylate group.

All the products listed in Table I are known compounds and were characterized by boiling points, melting points, densities, and, where appropriate, by the melting points of 2,4-dinitrophenylhydrazone and/or oxime derivatives.

#### EXPERIMENTAL<sup>9</sup>

**Materials.** With the exception of the five acids listed below, the carboxylic acids were purchased and purified prior to use either by redistillation and/or recrystallization. The iron was H reduced iron powder, produced by Fisher Scientific Co.

**Pentanoic acid.** Due to the wide boiling ranges of commercial pentanoic acids obtained from a variety of sources, pentanoic acid was prepared both by hydrolysis of butanenitrile and by carbonation of the Grignard reagent of 1-bromobutane, according to the procedures of Vogel.<sup>10</sup>

**Undecanoic acid.** Eighty-seven grams (0.47 mole) of redistilled (b.p. 273–275°) 10-undecenoic acid was dissolved in 200 ml. of 95% ethanol in a Parr pressure flask and reduced over 3 g. of Raney nickel catalyst<sup>11</sup> at 25° and 60 psi.

In 1.5 hr., 97% of the theoretical amount of hydrogen was absorbed. Following removal of catalyst and solvent, 65.3 g. (74%) of undecanoic acid, b.p. 166–168° at 11 mm., m.p. 24.0–24.5°, was obtained by distillation *in vacuo*. (Reported<sup>12</sup> m.p. 28.5°; reported<sup>13</sup> b.p. 168° at 11 mm.)

**3-Phenylpropanoic acid.** This material was prepared in 93% yield by the reduction of 3-phenyl-2-propenoic acid in a manner similar to that reported above for the preparation of undecanoic acid; m.p. 47–48° (reported<sup>14</sup>, m.p. 47–48°).

**4-Phenylbutanoic acid.** This substance was prepared from 3-benzoylpropanoic acid<sup>14</sup> by use of a somewhat altered Huang-Minlon<sup>16</sup> modification of the Wolff-Kischner reduction. A solution of 5 g. (0.028 mole) of 3-benzoylpropanoic acid, 5 g. of potassium hydroxide, 7.5 ml. of 85% hydrazine hydrate, and 20 ml. of diethylene glycol was refluxed 1 hr., then 8.5 ml. of liquid was distilled from the reaction solution to raise the boiling point of the solution to 200°; the solution was refluxed for 3 hr. more. To the cool solution were added 24 ml. of water and 12 ml. of hydrochloric acid (sp. gr. 1.18); the solution was extracted with three 5-ml. portions of carbon tetrachloride. After treatment of the carbon tetrachloride solution with charcoal and Filter-aid, the solution was filtered and evaporated to yield 4.6 g. (100%) of colorless crystals, m.p. 49–50°. (Reported<sup>17</sup> m.p. 46–48°).

**Phenoxyethanoic acid.** This substance was prepared according to the procedure of Koelsch.<sup>18</sup>

**General decarboxylation procedure.** A quantity of the appropriate carboxylic acid from 0.1 mole to 1.0 mole, was mixed with an equivalent plus 10% (0.055 to 0.55 mole) of H reduced iron powder in a round bottom flask. A thermometer was suspended in the mixture through a condenser attached to the flask. A gas delivery tube led from the top of the condenser through an Ascarite tube (to absorb carbon dioxide) and thence to a test tube containing water to serve as a bubble counter. In some experiments the volume of hydrogen evolved was determined by collecting the hydrogen by water displacement from inverted glass cylinders placed in a reservoir of water. The volume of hydrogen collected in all instances was within 5% of the theoretical, regardless of the yield of ketone finally obtained.

The mixture of iron and acid was refluxed until hydrogen evolution ceased; 1 to 3 hr. were required for complete reaction of iron and acid. In those instances where the boiling point of the acid and ketone were below the decomposition temperature of the salt, the mixture was cooled and protected from air by dry nitrogen while the flask was set for

(6) O. Neunhöfer and P. Pascke, *Ber.*, **72**, 919 (1939).

(7) R. Curtis, A. Dobson, and H. Hatt, *J. Soc. Chem. Ind.*, **66**, 402 (1947).

(8) A. Miller, N. Cook, F. Whitmore, *J. Am. Chem. Soc.*, **72**, 2732 (1954).

(9) All temperatures are uncorrected.

(10) A. Vogel, *A Textbook of Practical Organic Chemistry*, Green, New York, 1954, p. 353; p. 355.

(11) R. Mazingo, *Org. Syntheses*, Coll. Vol. III, 181 (1955).

(12) F. Krafft, *Ber.*, **11**, 2219 (1878).

(13) P. Bagard, *Bull. soc. chim. France*, (4)1, 353 (1907).

(14) V. Grignard, *Compt. rend.*, **138**, 1049 (1904).

(15) L. Somerville and C. Allen, *Org. Syntheses*, Coll. Vol. II, 81 (1943).

(16) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(17) E. Martin, *Org. Syntheses*, Coll. Vol. II, 500 (1943).

(18) C. Koelsch, *J. Am. Chem. Soc.*, **53**, 304 (1931).

downward distillation. Distillation was continued until no further volatile material evolved.

For those acids and ketones of boiling point above the decomposition temperature of the iron(II) carboxylates, the reflux apparatus was retained following cessation of the evolution of the hydrogen. The Ascarite tube was removed from the gas delivery train and refluxing was continued until evolution of carbon dioxide ceased. Usually 1 hr. sufficed for complete decarboxylation of the iron(II) carboxylate.

At this point the flask was set for downward distillation and the crude ketone distilled from the reaction mixture.

The crude ketone was shaken with a saturated solution of sodium hydrogen carbonate to remove traces of unreacted acid, then dried with silica gel and redistilled, or recrystallized from ethanol, or ethanol and water, depending upon the properties of the product.

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## Decarboxylation Studies. II. Preparation of Alkyl Phenyl Ketones<sup>1,2</sup>

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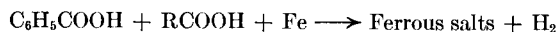
A recently published study<sup>1</sup> of the preparation of symmetrical, straight chain, aliphatic ketones has been extended to a study of the preparation of alkyl phenyl ketones by the thermal decarboxylation, in the liquid phase, of iron salts of mixtures of aliphatic and aromatic carboxylic acids. To the references recorded in the earlier publication<sup>1</sup> should be added the work of

(1) Paper I of this series: R. Davis and H. P. Schultz, *J. Org. Chem.*, **27**, 854 (1962).

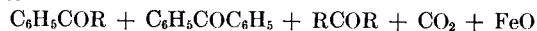
(2) Abstracted in part from the M.S. thesis of C. G., University of Miami, 1962.

Friedel,<sup>3</sup> who reported the first synthesis of an alkyl phenyl ketone, acetophenone, by pyrolysis of a mixture of calcium benzoate and calcium acetate. Other than this, alkyl phenyl ketones have been prepared by pyrolysis reactions<sup>4</sup> in the vapor state only.

The reaction may be formulated as follows:



Ferrous salts  $\longrightarrow$



The nature of the iron(II) salt has been discussed in the earlier work.<sup>1</sup> Although three ketones may possibly be obtained, this study demonstrated that the above reaction yielded mainly the alkyl phenyl ketone and little or no dialkyl ketone or benzophenone.

Fifteen representative aliphatic acids were treated with benzoic acid and iron in equimolar ratios. The alkyl phenyl ketones in the crude reaction mixtures were determined quantitatively from the ultraviolet absorption spectra by comparison with the spectra of known, pure standards; the reaction mixtures then were purified by traditional methods. Because of ease of isolation, the yields of methyl, ethyl, isopropyl, and secondary butyl phenyl ketones were not determined spectroscopically. *n*-Hexyl, *n*-heptyl, and *n*-octyl phenyl ketones have yield data based solely on spectroscopic data, because of similarity of boiling points, melting points, and solubilities of alkyl phenyl ketone and corresponding dialkyl ketone. Table I summarizes these data.

TABLE I

YIELDS OF ALKYL PHENYL KETONES BY PYROLYSIS OF IRON SALTS OF MIXED BENZOIC ACID AND ALIPHATIC CARBOXYLIC ACIDS

Alkyl substituent	Yield, %, of phenone		Weight % phenone in crude product, analyzed
	Analyzed	Isolated	
Methyl	—	33	—
Ethyl	—	50	—
<i>n</i> -Propyl	69	48	90
Isopropyl	—	69	—
<i>n</i> -Butyl	62	55	81
<i>sec</i> -Butyl	—	69	—
<i>n</i> -Pentyl	73	65	86
<i>n</i> -Hexyl	73	—	82
<i>n</i> -Heptyl	69	—	90
<i>n</i> -Octyl	70	—	87
<i>n</i> -Nonyl	62	50	89
<i>n</i> -Undecyl	74	50	93
<i>n</i> -Tridecyl	76	64	92
<i>n</i> -Pentadecyl	78	66	90
<i>n</i> -Heptadecyl	69	52	74

The reaction of benzoic acid, propanoic acid, and iron was studied, varying the molar ratios of organic reactants. It was found (Table II) that increasing the ratio of one reactant over the other, from 1:1, increased the yield of alkyl phenyl ketone. An excess of

TABLE II

YIELDS OF PROPIOPHENONE BY PYROLYSIS OF IRON SALTS VARYING RATIOS OF BENZOIC ACID AND PROPANOIC ACID

Molar ratio		Yield, %, propiophenone isolated
Benzoic acid	Propanoic acid	
4	1	72
2	1	60
1	1	50
1	2	55
1	4	59

benzoic acid, however, had a more pronounced effect than an excess of propanoic acid.

Thirteen substituted benzoic acids were treated with propanoic acid and iron in equimolar ratios. A simplified, semimicro procedure was used so that a relatively large number of compounds could be screened efficiently. That some yield was sacrificed in this procedure may be noted by comparing the yields of propiophenone itself when obtained by the macro procedure (Table I) and the semimicro procedure (Table III). Propanoic acid was selected as the aliphatic acid for reaction with the substituted benzoic acids for these reasons: (1) No by-product 3-pentanone was observed in the reaction between propanoic acid and benzoic acid. (2) Propiophenone was obtained in 50% yield from the reaction between propanoic and benzoic acids; any change in yield, therefore, could be readily observed. (3) The expected nucleus-substituted propiophenones are all known compounds.

TABLE III

YIELDS OF NUCLEAR SUBSTITUTED PROPIOPHENONES FROM PYROLYSIS OF IRON SALTS OF SUBSTITUTED BENZOIC ACIDS AND PROPANOIC ACID

Aromatic substituent	Yield, %, substituted propiophenone isolated	
Hydrogen	39	
<i>o</i> -Methyl	0	
<i>m</i> -Methyl	22	
<i>p</i> -Methyl	27	
<i>o</i> -Chloro	0	
<i>m</i> -Chloro	42	
<i>p</i> -Chloro	20	
<i>o</i> -Nitro	0	
<i>m</i> -Nitro	0	
<i>p</i> -Nitro	0	
<i>p</i> -Amino	0	
<i>p</i> -Bromo	21	
<i>p</i> -Hydroxy	0	
<i>p</i> -Methoxy	27	

Data in Table III show an obvious *ortho* effect and also demonstrate that strongly positive or negative groups in the *meta* or *para* position interdict the ketonic decarboxylation. *meta*-Alkyl and *meta*-halogen substituted phenones are, however, more readily available from this reaction than *via* the traditional Friedel-Crafts reaction.

### Experimental

**Materials.**—All organic starting materials were purchased and purified prior to use by either distillation and/or recrystallization. The iron was hydrogen reduced iron powder, produced by Fisher Scientific Company.

(3) C. Friedel, *Jahresber. Fortschr. Chem.*, 270 (1857); F. K. Beilstein, "Handbuch der organischen Chemie," Vol. 7, 4th ed., B. Prager, P. Jacobson, P. Schmidt, and D. Stern, ed., J. Springer Verlag, Berlin, 1925, p. 272.

(4) J. B. Senderens, *Compt. rend.*, 150, 112, 702 (1910); M. A. Mailhe, *ibid.*, 157, 220 (1913); P. Sabatier and M. A. Mailhe, *ibid.*, 158, 830 (1914).

TABLE IV  
ULTRAVIOLET ABSORPTION DATA IN CYCLOHEXANE OF PURE  
ALKYL PHENYL KETONES

Alkyl moiety	$\lambda_{\max}$ , m $\mu$	$\epsilon \times 10^{-4}$
<i>n</i> -Propyl	240	1.11
<i>n</i> -Butyl	240	1.12
<i>n</i> -Pentyl	239	1.30
<i>n</i> -Hexyl	239	1.34
<i>n</i> -Heptyl	240	1.20
<i>n</i> -Octyl	240	1.16
<i>n</i> -Nonyl	236	1.80
<i>n</i> -Undecyl	239	1.29
<i>n</i> -Tridecyl	236	1.72
<i>n</i> -Pentadecyl	240	1.26
<i>n</i> -Heptadecyl	240	1.09

**Preparation of Pure Alkyl Phenyl Ketones as Analytical Standards.**—Table IV lists the alkyl phenyl ketones prepared by the Friedel-Crafts procedure of Breusch and Oguzer.<sup>5</sup>

**Preparation of Alkyl Phenyl Ketones.**—The apparatus has been described.<sup>1</sup> One tenth mole of benzoic acid, 0.1 mole of aliphatic acid, and 0.11 mole of iron were used in reactions with aliphatic carboxylic acids of less than five carbon atoms; twice these quantities were utilized in reactions involving aliphatic acids of five or more carbon atoms. The reaction flask was heated to 250° until hydrogen evolution (100% yield in all cases) ceased—approximately 45 min. If the expected alkyl phenyl ketone had less than nine carbon atoms in the side chain, the condenser was set for downward distillation, and the flask heated until distillation ceased. Evolution of carbon dioxide and distillation occurred at a pot temperature of 280–300°; only a few drops of black tar distilled at higher temperatures. The volatile distillate was diluted with ether, washed with saturated sodium bicarbonate solution, dried, concentrated, and weighed. An accurately weighed sample of 10 mg. of crude product was dissolved in 1 l. of cyclohexane and compared at the wave length of maximum absorption with the spectrum of the corresponding pure ketone. The alkyl phenyl ketone was then distilled to separate it from possible lower boiling dialkyl ketones. From the appropriate ketones no acetone, no 3-pentanone, no 2,4-dimethylpentanone-3, 12% of 4-heptanone, no 3,5-dimethylheptanone-4, and 8% yields of 5-nonanone were obtained. The tarry, nonvolatile, red residue remaining after twenty-five different distillations were combined to give 50 g. of material. Chromatographic study of the small amount of tar (about 4 g.) boiling at 300–400° indicated (infrared spectrum) some benzophenone to be present; no other materials were identified in the tar. (Parenthetically, it was observed that when only benzoic acid and powdered iron were treated, a pot temperature of 350–400° was required to decompose the iron(II) benzoate; yields of 13% benzene, 17% benzophenone, a trace of benzaldehyde, and much tar resulted.)

If the expected alkyl phenyl ketone had nine or more carbon atoms in the side chain, ketonic decarboxylation of the iron salts was effected with the condenser attached vertically to the decarboxylation flask. After decarboxylation, the impure ketone was dissolved in 200 ml. of ether, filtered through a pad of Celite to remove particles of iron and iron oxide, washed with sodium bicarbonate solution, dried, concentrated, weighed, and analyzed for alkyl phenyl ketone. The crude red residue was dissolved in cyclohexane (10 ml./g.) and passed through a 2.5 × 20 cm. column of alumina, eluting the column with a double volume of cyclohexane. After the removal of solvent, the colorless, solid residue was recrystallized one to three times from 95% ethanol to give pure alkyl phenyl ketone.

The identity and purity of products were established by boiling and/or melting points, melting points of 2,4-dinitrophenylhydrazones and/or semicarbazones, and quantitative ultraviolet absorption spectra.

**Semimicro Preparation of Ethyl Substituted Phenyl Ketones.**—

Into a 200-cm. test tube equipped with condenser, drying tube, and bubble counter were placed 0.05 mole of propanoic acid, 0.05 mole of substituted benzoic acid, and 0.054 mole of powdered iron. The tube was heated in an electric coil at 280–300° until all gas evolution ceased. No attempt was made to distil ketone

as it formed. The cooled tube was broken directly into a steam distillation flask containing 500 ml. of water and 10 g. of sodium bicarbonate. After steam distillation, the distillate was extracted with chloroform, then dried, concentrated, and distilled and/or recrystallized, depending upon the properties of the expected ketone.

(5) F. L. Breusch and M. Oguzer, *Chem. Ber.*, **87**, 1227 (1954).