When a 1-g sample of the mixture of olefins **20a**–**20b** 50:1 was heated with an increased amount of trifluoroacetic acid (5 ml) for 36 hr, a 700-mg mixture of distilled sample of **24**–**25** 37:63 was obtained. A 200-mg distillation residue was also obtained. The ratio of products was obtained from gas chromatographic analysis on column A and from the nmr spectrum of the mixture.

Hydrogenation of 20c to 23.—A sample of **23** was prepared by hydrogenating 500 mg of **20c** in the presence of 100 mg of Pd/C catalyst in ethyl acetate solvent. After the hydrogenation was complete, the catalyst was filtered out and ethyl acetate was removed to give 400 mg of colorless liquid. Gas chromatographic analysis of the product on column A gave a single peak. The nmr spectrum showed peaks at 6.65 (2 H, s), 2.51 (2 H, m), 2.20 (6 H, s), 2.16 (3 H, s), 1.67 (1 H, m), 1.32 (2 H, m), and 0.98 ppm (3 H, d).

Registry No.—Isoprene, 78-79-5; **8,** 1078-04-2; **11,** 16204-57-2; **12,** 16204-58-3; **13,** 942-43-8; **17,** 941-60-6; **20a,** 16204-61-8; **20c,** 16204-62-9; 21, 5344-18-3; **22,** 16204-64-1; **23,** 16204-65-2; **24,** 6682-67-3; **25,** 16204-67-4; **26,** 10425-83-9; **27,** 16204-69-6; **31,** 16204-70-9; **32,** 14276-95-0; **33,** 16204-72-1; **38,** 3605-31-0; **39,** 16204-73-2; **20b,** 16204-74-3.

Acknowledgments.—We are grateful to the American Petroleum Institute for their generous support of this research. We thank Dr. O. C. Dermer for reading the manuscript and for stimulating discussions. We also thank the personnel of the Research Foundation, Oklahoma State University, for their assistance.

Oxidative Decarboxylation of γ-Oxo Acids Using Lead Dioxide

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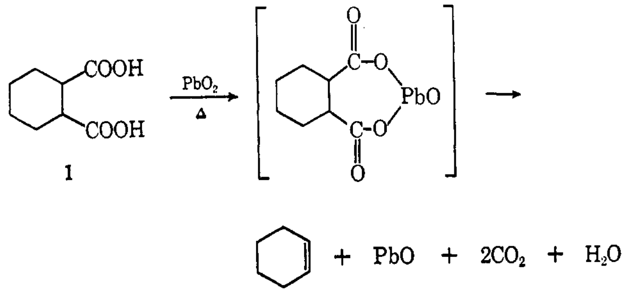
Received October 11, 1967

The oxidative decarboxylation of γ-oxo acids to α,β-unsaturated ketones with lead dioxide is shown to be a general reaction with best yields realized from acids substituted at the α and/or β carbon atom. The techniques developed provide a unique means of preparing α,β-unsaturated ketones in yields up to 84% using commercially available lead dioxide. The procedure may be applied to milligram amounts.

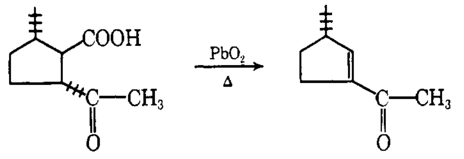
The elimination of vicinal dicarboxylic acid and anhydride functions to yield a double bond at the site [*e.g.*, formation of cyclohexene (**2**) from cyclohexane-1,2-dicarboxylic acid (**1**)] may be effected with hot lead dioxide.[2]



1 **2**

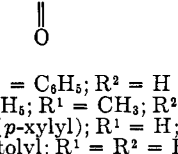
Grob, *et al.*, substituted lead tetraacetate in pyridine for lead dioxide.[3] This and later modifications have essentially supplanted oxidative decarboxylation with lead dioxide, probably because higher yields, lower temperature, and better control over the reaction have been reported repeatedly.[4,5] In general, lead tetraacetate decarboxylations give the same olefinic products.

In 1955, one of us demonstrated that (−)-3-methylcyclopenten-1-yl methyl ketone (**4**) was the major product of lead dioxide oxidative decarboxylation of nepetonic acid (**3**).[6] These observations have now been confirmed. The decarboxylation of γ-oxo acids with lead dioxide is strikingly different from the reaction of vicinal dicarboxylic acids with hot lead dioxide.

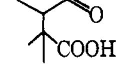


3 **4**

We have extended this earlier work to other γ-oxo acids. The reaction appears to be general, but the yield of α,β-unsaturated ketone usually does not exceed 30–40% for γ-oxo acids having no alkyl or aryl substituents at the α or β position. The best yields were obtained from the α-phenyl-γ-oxo acid **5a** and the α,α-dimethyl-γ-oxo acid **6**, which gave the corresponding α,β-unsaturated ketones in 84 and 76% yields, respectively. A 72% yield was realized from 3-methyl-3-(2,5-dimethylbenzoyl)propionic acid (**5c**), which is substituted in the β position. However, acid **5d**, with no alkyl or aryl substituents in the α or β position, gave a mixture of six products in low yield.



$\mathrm{Ar\overset{\|}{\underset{\|}{C}}\overset{R^2}{\underset{}{C}}H\overset{R^1}{C}HCOOH}$, with O under the first C



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5a, Ar = R^1 = C$_6$H$_5$; R^2 = H
b, Ar = C$_6$H$_5$; R^1 = CH$_3$; R^2 = H
c, Ar = 2-(*p*-xylyl); R^1 = H; R^2 = CH$_3$
d, Ar = *p*-tolyl; R^1 = R^2 = H
e, Ar = 2-(*p*-xylyl); R^1 = CH$_3$; R^2 = H
f, Ar = 2-naphthyl; R^1 = C$_6$H$_5$; R^2 = H
g, Ar = 2-naphthyl; R^1 = CH$_3$; R^2 = H
h, Ar = 1-naphthyl; R^1 = R^2 = H

The potential of this reaction for the preparation of α,β-unsaturated ketones in the degradation of natural products can best be appreciated when we include γ-lactones, which may be converted into γ-oxo acids.

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[1] (a) National Science Foundation Research Participant for College Teachers during the summers of 1964 and 1965. (b) Address correspondence and requests for reprints to this author.

[2] W. von E. Doering, M. Farber, and A. Sayigh, *J. Amer. Chem. Soc.*, **74**, 4370 (1952).

[3] C. A. Grob, M. Ohta, and A. Weiss, *Angew. Chem.*, **70**, 343 (1958).

[4] C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

[5] N. B. Chapman, S. Sotheeswaran, and K. J. Toyne, *Chem. Commun.*, 214 (1965).

[6] S. M. McElvain and E. J. Eisenbraun, *J. Amer. Chem. Soc.*, **77**, 1599 (1955).

The high yields possible with α- and/or β-substituted acids in this one-step decarboxylation, in addition to the ease of product isolation, make lead dioxide a preferred decarboxylating agent.

The oxidative decarboxylations were carried out by one of four techniques. Our best yields were realized with method A, in which an intimate mixture of commercially available lead dioxide, the γ-oxo acid, and powdered soft glass are added to a sublimation tube. The tube is evacuated and then inserted part way into a preheated sublimation apparatus. Reaction takes place immediately and the product, an α,β-unsaturated ketone in this case, distills out of the reaction mixture and condenses in a cooled portion of the tube. The entire operation requires approximately 10 min.

Method B also utilizes a hot tube containing lead dioxide. A solution of the γ-oxo acid in xylene is added slowly to the hot lead dioxide to cause decarboxylation. The α,β-unsaturated ketone is washed from the lead dioxide into a receiving flask.

Method C, involving a suspension of lead dioxide in a boiling solution of γ-oxo acid in xylene, was found to be less convenient and produced lower yields.

Decarboxylation can also be effected and the product analyzed in a single operation by injecting a solution of the γ-oxo acid into a hot plug of lead dioxide inside the injection port and at the entrance of a gas chromatography column. The α,β-unsaturated ketone, impurities, and side products are swept by a helium stream through the gas chromatography column and recorded as peaks on the chromatogram.

Earlier studies[6] were carried out with granular lead dioxide of the type formerly used by microanalysts in the universal combustion tube filling according to Pregl.[7] This grade of lead dioxide is no longer commercially available.[8]

Variation in activity of lead dioxide from different sources was encountered with different reaction methods, particularly B and C. Doering and Finkelstein[9] and others[10] reported that commercial lead dioxide was not effective in the decarboxylation of some 1,2-dicarboxylic acids. A method for preparing activated lead dioxide was developed,[9] and indeed we have found that lead dioxide so prepared shows increased activity in methods B and C, but it does not approach the effectiveness of the original sample[6] of lead dioxide. Sufficient lead dioxide remained in the original bottle to permit direct comparisons.

We initially studied decarboxylation using methods B and C. However, the low yields encountered with commercial lead dioxide necessitated development of method A, which works satisfactorily with all samples of lead dioxide tried. The oxo acid **5a** used with a variety of lead dioxide samples in method A gave a 76–78% yield of 2′,5′-dimethylcrotonophenone (**7a**) in all cases.[11a] An even higher yield, 84%, of chalcone (**7b**) was obtained when 3-benzoyl-2-phenylpropionic acid (**5a**) was used.[11b]

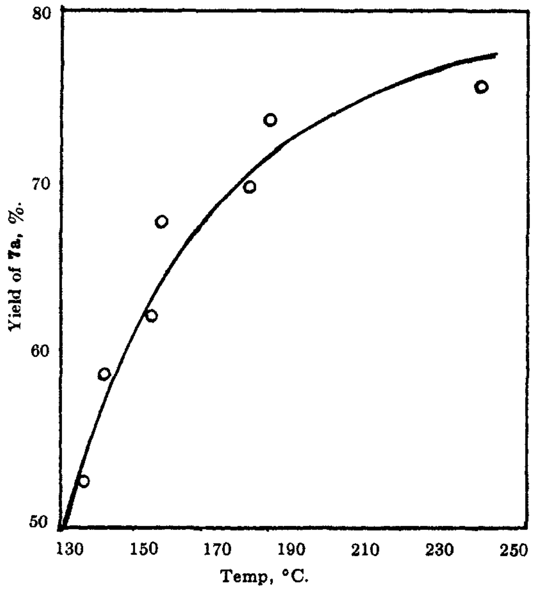
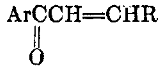


Figure 1.—Response of yield to reaction temperature for decarboxylation of **5e**.



$$\mathrm{Ar\overset{}{\underset{\underset{O}{\|}}{C}}CH{=}CHR}$$

7a, Ar = 2-(*p*-xylyl); R = CH_3
b, Ar = R = C_6H_5

The effect of temperature on the oxidative decarboxylation of the γ-oxo acid **5e** by method A is shown in Figure 1. For γ-oxo acids yielding products of low volatility, a reaction temperature of 250° is recommended since an immediate reaction takes place in high yield. However, γ-oxo acids yielding more volatile products and the half-esters **8** and **9** as well as the dicarboxylic acid **1** gave higher yields of decarboxylated material at 135°. In these latter cases, the higher temperature caused formation of cyclohexanedicarboxylic anhydride which sublimed out of the reaction tube.

Safety precautions should be observed during oxidative decarboxylation of γ-oxo acids with lead dioxide. The most serious hazard results from admitting air to the hot residue from a lead dioxide decarboxylation. This hazard is most pronounced in method A. Such contact invariably causes some sort of vigorous reaction, due presumably to pyrophoric particles, ranging from formation of sparks to violent explosions, which in one instance sounded like a shotgun blast and completely demolished a multipiece glass apparatus. The residue from this explosion was a hard lump which resembled lead metal. The experimental methods described are the result of considerable effort to develop safe reaction techniques, and no explosions should be encountered if proper precautions are observed. Insufficient mixing of γ-oxo acid, lead dioxide, and powdered glass may lead to a reaction mixture containing high local concentrations of acid which we believe may also be a cause of the more violent reactions. These reactive centers may be observed as dark spots in an otherwise uniformly yellow-brown reaction residue. Reactions which generate these dark spots usually produce lower yields of α,β-un-

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(7) J. B. Niederl and V. Niederl, "Organic Quantitative Microanalysis," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 122.

(8) Dr. Karl Pfister, III, Merck Sharp and Dohme, in a personal communication to E. J. E., Jan 19, 1959.

(9) W. von E. Doering and M. Finkelstein, *J. Org. Chem.*, **23**, 141 (1958).

(10) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *J. Amer. Chem. Soc.*, **77**, 594 (1954).

(11) (a) The lead dioxide samples used were Merck Reagent Grade, Baker's Analyzed Chemically Pure, Frank W. Kerr Co., Reagent Grade, and lead dioxide prepared by the method of Doering and Finkelstein. (b) The last two samples in ref 11a were used.

TABLE I

DECARBOXYLATION OF γ-OXO ACIDS TO α,β-UNSATURATED KETONES

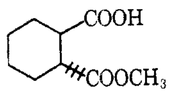
Acid	Product	Method[a]	Moles × 10^{-2} Acid	Moles × 10^{-2} PbO_2	Powdered glass, g	Xylene, ml	Reaction temp, °C	Reaction time, hr	Yield, %	Mp of 2,4-DNP, °C
5a	Chalcone (**7b**)	C	10.0	40.0	...	50	144	10.0	37	241–244[b]
		B	10.0	40.0	...	120	135	3.0	57	244[b]
		A	0.5	2.5	3	...	250	0.25	84	245[b]
5b	Crotonophenone	C	10.0	40.0	...	75	135	4.5	37	194–197[c]
		A	2.0	10.0	12	...	250	0.5	69	200–201[c]
5c	2,2′,5′-Trimethylacrylophenone	A	0.5	2.5	3	...	250	0.5	72	118
5e	2′,5′-Dimethylcrotonophenone (**7a**)	A	0.5	2.5	3	...	250	1.0	76	210–211
5f	3-Phenyl-2′-acrylonaphthone, mp 105–106°[d]	B	3.8	40.0	...	200	125	4.0	40	
		A	0.5	2.5	3	...	250	0.25	83	
5g	2′-Crotononaphthone	C	5.0	20.0	...	50	144	2.0	36	
		A	0.5	2.5	3	...	250	0.25	35	205[e]
6	Pulegone	B	5.0	40.0	...	50	135	2.0	11	
		A	0.5	2.5	3	...	250	1.0	76	142[f]
10	1-Cyclohexenyl methyl ketone	B	10.0	40.0	...	10	135	2.0	22	196–201[g]
		A	0.5	2.5	3	...	250	0.5	45	202–203[g]
13	2-Cyclohexen-1-one	A	2.0	10.0	12	...	250	0.5	92	163–165[h]

[a] See Experimental Section for decarboxylation procedures. [b] 245°, C. H. F. Allen and J. H. Richmond, *J. Org. Chem.*, **2,** 224 (1937). [c] 204°, V. Franzen, *Ann.*, **602,** 199 (1957). [d] 105–106°, A. Maccioni and E. Marongui, *Ann. Chim.* (Rome), **50,** 1806 (1960). [e] 214°, F. Ramirez and M. B. Rubin, *J. Amer. Chem. Soc.*, **77,** 2905 (1955). [f] 142°, O. L. Brady, *J. Chim. Soc.*, 758 (1931). [g] 202–203°, D. Nightingale, E. C. Milberger, and A. Tomisek, *J. Org. Chem.*, **13,** 357 (1948). [h] 163°, P. D. Bartlett and G. F. Woods, *J. Amer. Chem. Soc.*, **77,** 2905 (1955).

saturated ketones. The mixing at ordinary temperatures is without hazard. We caution against exceeding *reported* limits without extensive trial.

The presence of the ketone function in the γ-oxo acids being decarboxylated is essential to high yields of α,β-unsaturated ketones. The half-esters **8** and **9** of the 1,2-cyclohexanedicarboxylic acids on reaction with hot lead dioxide give a low yield (*ca.* 12–15%) of a complex mixture of unsaturated esters while **10**, the γ-oxo analog of **8**, provides a 45% yield of 1-cyclohexenyl methyl ketone under the same conditions. Decarboxylation of other acids without the ketone function generated extremely complex mixtures of products. Evidently the role of the ketone carbonyl is not limited to resonance stabilization of the double bond formed.

The inability of the enol lactones **11** and **12** to form significant products in the lead dioxide decarboxylation reaction indicates that these easily formed derivatives of γ-oxo acids do not have a role in the decarboxylation mechanism.



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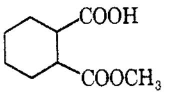

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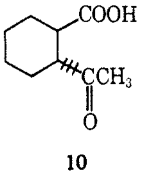

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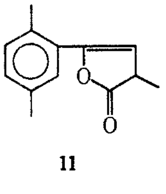

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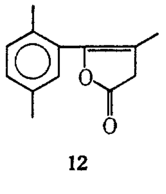
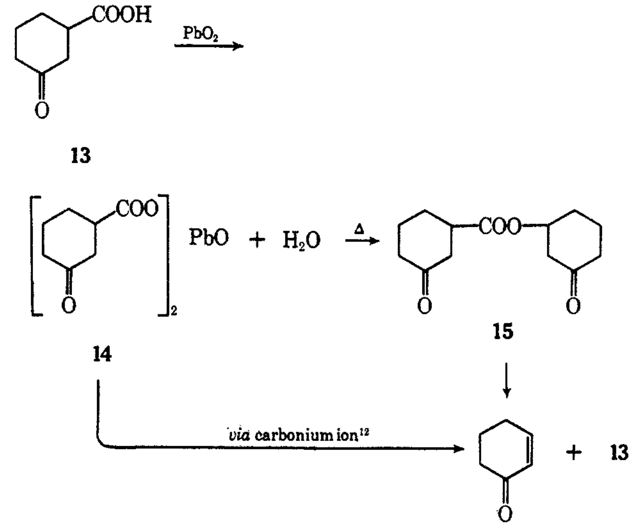


12

The effect of α substitution on the yield of α,β-unsaturated ketones from γ-oxo acids can be seen in the series of β-aroylpropionic acids **5a**, **5b**, **5d**, **5f**, **5g**, and **5h**. Those acids substituted in the α position gave the α,β-unsaturated ketones in 70–85% yields with only minor impurities. Those acids without substitution in the α or β position, **5d** and **5h**, gave low yields of complex mixtures of products. The β-substituted acid **5c** was oxidatively decarboxylated with lead dioxide to give the α,β-unsaturated ketone in 72% yield (*cf.* Table I).

The heterogeneous nature of these reactions presents obvious difficulties in studying the mechanism. The instability of an α,β-unsaturated ketone or occurrence of side reactions could give misleading results. Until better methods of study are available, it will be necessary to rely on product analysis to gain an insight into the reaction mechanism. The evidence suggests a reaction mechanism similar to that proposed by Kochi for the lead tetraacetate decarboxylation of aliphatic acids.[12,13] This applied to oxo acid **13** would involve homolytic cleavage of the lead salt **14** and decarboxylation to an alkyl radical which, if stabilized by electron-donating groups, would further react to form alkenes and esters such as **15**.[14] An unsubstituted free radical would produce a complex mixture typical of free radical products.



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(12) J. K. Kochi, *J. Amer. Chem. Soc.*, **87**, 1811 (1965).

(13) D. I. Davies and C. Waring, *Chem. Commun.*, 263 (1965).

(14) We thank a referee for valuable suggestions regarding this rationalization.

The high yield of α,β-unsaturated ketone from **5c** is not consistent with the Kochi mechanism, but more examples will be required to clarify this point.

The results of various lead dioxide decarboxylations of γ-oxo acids are summarized in Table I. We are continuing our investigation of the use of lead dioxide in oxidative decarboxylation of γ-oxo acids and related molecules to clarify the mechanism of the reaction and evaluate its utility in degradation and synthesis of organic molecules.

Experimental Section

Preparation of Starting Materials.—2-Phenyl-3-benzoylpropionic acid (**5a**), 2-phenyl-3-(2-naphthoyl)propionic acid (**5f**), *p*-menthan-3-one-8-carboxylic acid (**6**), and 2-acetylcyclohexanecarboxylic acid (**10**) were obtained by adding cyanide ion[15] to appropriate α,β-unsaturated ketones and subsequently hydrolyzing to the γ-oxo acids. The α,β-unsaturated ketones were prepared by heating Mannich bases,[16] by Claisen–Schmidt condensation,[17] or by Friedel–Crafts acylation of olefins.[18] 2-Methyl-3-benzoylpropionic acid (**5b**) and 2-methyl-3-(2-naphthoyl)propionic acid (**5g**) were prepared by reaction of benzene or naphthalene with methylsuccinic anhydride in the presence of aluminum chloride.[19] The preparations of **5c** and **5e** and the enol lactones **11** and **12** are described elsewhere.[20] 3-(*p*-Toluoyl)propionic acid (**5d**) was obtained from the Aldrich Chemical Co. and used without further purification.

The *monomethyl* esters of *cis*- and *trans*-1,2-cyclohexanedicarboxylic acids were prepared from 25 g (0.162 mol) of cyclohexanedicarboxylic anhydride and 9.12 g (0.286 mol) of methanol, which were heated together at the reflux temperature for 4 hr. The methanol was distilled at reduced pressure to give a clear residue which was extracted with 160 ml of 10% sodium bicarbonate. After three extractions with 25-ml portions of methylene chloride, the aqueous layer was acidified. The acidic solution was extracted three times with 25-ml portions of methylene chloride and the methylene chloride extracts were combined and dried over anhydrous magnesium sulfate, filtered, and evaporated. Crystals formed after 5 days at room temperature. Recrystallization of half the material in petroleum ether gave 4.82 g of the monomethyl ester of *cis*-1,2-cyclohexanedicarboxylic acid, mp 66.5–68° (lit.[21] mp 68–69°). Distillation of the other half of the reaction product at 100° (0.6 mm) produced only cyclohexanedicarboxylic anhydride and methanol in the distillate, but recrystallization of the undistilled material in petroleum ether (bp 60–80°) yielded 0.98 g of the monomethyl ester of *trans*-1,2-cyclohexanedicarboxylic acid, mp 93–95° (lit.[22] 95–96°).

Decarboxylation of γ-Oxo Acids.—All the γ-oxo acids were decarboxylated by one of the four following methods. Yields of products and methods of preparation are listed in Table I. A specific γ-oxo acid decarboxylation is described for each method.

The reaction products were identified by infrared absorption at 1690 and 1620 cm^{-1} (representing the conjugated carbonyl and double bond, respectively), gas chromatography, and preparation of 2,4-dinitrophenylhydrazones. In some cases, gas chromatographic analysis showed the presence of minor impurities (*ca.* 1–5%).

A. Hot Tube with Powdered Soft Glass.—A mixture of 3 g of powdered soft glass, 0.110 g (5.0×10^{-4} mol) of **5e**, and 0.598 g (2.5×10^{-3} mol) of lead dioxide were ground in a mortar and placed in a 9-mm Pyrex tube closed at one end. After a glass wool plug was placed over the loosely packed mixture, the tube was evacuated to about 0.5 mm and partially inserted horizontally in an aluminum block preheated to 250°. A 5-cm portion of the tubing outside the aluminum block was cooled in powdered Dry Ice. After 10 min, the reaction appeared to be complete. The product collected before the Dry Ice cooled portion of the tube just outside the sublimer. The portion of the tube which contained the product was broken away from the rest to give 0.066 g (76%) of **7a**, bp 90° (0.3 mm). The infrared spectrum of the yellow liquid showed absorption at 1656 and 1625 cm^{-1}, indicating a conjugated carbonyl group and double bond. The lack of absorption at 1715 cm^{-1} indicates the absence of a carboxyl group. Analysis by gas chromatography[23] showed the product to be free of impurities.

The nmr spectrum of **7a** showed δ 7.11 (1 aromatic H, singlet), 7.01 (2 equivalent aromatic H, s), 6.47 (1 vinylic H, s), 6.63 (1 vinylic H, quartet decoupled at 6.63), 2.27 (6 methyl H, s) and 1.813–1.900 (3 methyl H, doublet). An intense parent ion was observed at *m/e* 174 and the six most intense peaks appeared at *m/e* 159, 133, 105, 39, 77, and 41.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.73; H, 8.21.

Application of method A to **5c** gave 2,2′,5′-trimethylacrylophenone, bp 64° (0.3 mm), in 72% yield. The nmr spectrum showed 6.97 (3 aromatic H, multiplet), 5.81 (1 vinylic H, m), 5.47 (1 vinylic H, m), 2.23 (3 methyl H, singlet), 2.16 (3 methyl H, s), and 1.95 (1 vinylic H, m). The mass spectrum showed an intense parent ion at *m/e* 174 and the six most intense peaks were observed at *m/e* 159, 133, 174, 105, 39, and 77.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.85; H, 7.73.

Comparison of the Use of Pyrex Glass and Soft Glass in Method A.—A mixture of 0.220 g (0.001 mol) of **5e**, 0.957 g (0.004 mol) of lead dioxide, and 2 g of powdered Pyrex glass was heated according to method A at 135° to give the α,β-unsaturated ketone in 40% yield (0.070 g). Substitution of powdered soft glass for the Pyrex glass gave the same product in 42% yield. Doubling the quantity of soft glass raised the yield to 46% (0.080 g).

B. Hot Tube with Solvent.—Lead dioxide (9.600 g, 0.040 mol) was placed between glass wool plugs in a vertical 9-mm Pyrex tube which passed through an aluminum heating block. The top of the tube was fitted with a dropping funnel and the bottom with a receiver side arm flask immersed in an ice bath. Nitrogen was passed through the system as the lead dioxide was heated to 135°. A solution of 2.540 g (0.010 mol) of **5a** in 120 ml of *o*-xylene was dripped through the lead dioxide at a rate of 1 drop every 4–6 sec. After all the acid had been added, the lead dioxide was washed with 50 ml of *o*-xylene and the combined xylene solutions were extracted twice with 20-ml portions of 10% sodium bicarbonate and once with 20 ml of distilled water. The bright yellow nonaqueous solution was dried over magnesium sulfate and filtered and the xylene largely removed by distillation at reduced pressure. The remainder of the xylene was separated from the product by chromatography through a column of Merck acid-washed alumina. The column was washed with 50 ml of hexane and the product eluted with 150 ml of benzene. The benzene solvent was distilled at reduced pressure, leaving a yellow oily residue which crystallized on standing overnight. Recrystallization from ethanol gave 1.180 g (57%) of chalcone (**7b**) as yellow needles melting at 53–55° (58°).[24]

The aqueous bicarbonate solution was acidified and extracted three times with ether. The ether layer was dried over magnesium sulfate, filtered, and evaporated to give 0.398 g of unreacted acid melting at 148–150°. The yield based on recovered acid was 67%.

C. Refluxing Solvent Method.—In a 200-ml flask were placed 1.920 g (0.010 mol) of **5b**, 9.600 g (0.040 mol), of lead dioxide and 75 ml of xylene. Nitrogen was passed through the apparatus at room temperature for 1 hr. The mixture was agitated with magnetic stirring and heated at reflux for 4.5 hr. After cooling and filtering, the xylene was distilled at reduced pressure, the liquid residue was dissolved in ether, and the ether solution was

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washed with a saturated sodium bicarbonate solution and a saturated salt solution and dried over anhydrous magnesium sulfate. Distillation of the ether through a spiral column left a residue which was treated with 2,4-dinitrophenylhydrazine reagent.[25] The red precipitate was purified by elution through alumina with benzene and distillation of the benzene at reduced pressure to give crystals of the 2,4-dinitrophenylhydrazone of crotonophenone in 37% yield (1.213 g) melting at 194–197° (*cf.* Table I).

D. **On-Column Reaction.**—A 0.2-g plug of lead dioxide between glass wool plugs was placed in the injection port of an F & M Model 700 gas chromatograph. A dilute solution (100 μl of 10^{-3} *M*) of a γ-oxo acid in ether was injected directly into the lead dioxide plug. The yield of α,β-unsaturated ketone produced was determined by comparing the peak area with those found for known amounts of the product.

With the injection port at 200° a 30% yield of **7b** was realized from acid **5a** while the α,β-unsaturated ketones derived from acids **5c** and **5e** were detected in 20% yields. In each case none of the enol lactone which would be formed by unreacted acid was found. Examination of the lead dioxide plugs after reaction showed very little charring.

Decarboxylation of Other Compounds. ***cis*-1,2-Cyclohexanedicarboxylic Acid.**—A mixture of 0.100 g (5.8×10^{-5} mol) of **1**, 0.557 g (2.33×10^{-4} mol) of lead dioxide, and 5 g of powdered Pyrex glass was heated at 135° by method A above. The product was collected along with water in the cooled portion of the tube. After 1 hr reaction time, the product was taken up in ether, and the ether layer dried over anhydrous magnesium sulfate and evaporated to give 0.021 g (44% yield) of cyclohexene. The infrared spectrum of the product was identical with that of reagent grade cyclohexene.

The Enol Lactone of 2-Methyl-3-(2,5-dimethylbenzoyl)propionic Acid (11).—A mixture of 0.202 g (0.001 mol) of **11**, 0.957 g (0.004 mol) of lead dioxide, and 2 g of powdered Pyrex glass was heated, using method A, at 135° for 1 hr. The only material other than water which collected in the tube was 0.015 g of unreacted starting material. However, the lead dioxide had turned yellow, indicating that a reaction occurred.

The Enol Lactone of 3-Methyl-3-(2,5-dimethylbenzoyl)propionic Acid (12).—A mixture of 0.404 g (0.002 mol) of **12**, 2.392 g (0.010 mol) of lead dioxide, and 12 g of powdered soft glass was allowed to react according to method A at 250° for 15 min. Material condensed in two zones, ahead of the sublimer and also in the portion of the tube cooled with Dry Ice. Analysis by gas chromatography and infrared spectroscopy showed the former to be unreacted enol lactone while the latter was a 7-mg mixture of six compounds, one of which was the α,β-unsaturated ketone in about 0.1% yield.

***trans*-1,2-Cyclohexanedicarboxylic Acid, Monomethyl Ester (8).**—A mixture of 0.20 g (1.8×10^{-4} mol) of **8**, 1.03 g (4.3×10^{-3} mol) of lead dioxide, and 2 g of powdered Pyrex glass was treated at 135° by method A. The products condensed in three zones outside the sublimer and were separated by breaking the tubing between each pair of zones. Unreacted starting material (0.221 g) and 0.005 g of the anhydride of 1,2-cyclohexanedicarboxylic acid were isolated from the first two zones and were identified by a comparison of the infrared spectra with those of standard samples. In the third zone, 0.0203 g of material appeared; it showed no carboxyl group absorption in its infrared spectrum between 2500 and 2700 cm^{-1} but did have absorption bands at 1725 (ester function) and 1648 cm^{-1} (double bond). Gas chromatographic analysis showed the condensate to be a mixture of mainly three compounds which were not identified.

***cis*-1,2-Cyclohexanedicarboxylic Acid, Monomethyl Ester (9).**—The above procedure was applied to **9** to give 0.017 g of decarboxylated product with an infrared spectrum very similar to the product from the *trans* half-ester. Gas chromatography showed this material to be primarily three compounds but there were 17 peaks in all.

Registry No.—**5a**, 4370-96-1; **5b**, 1771-65-9; **5c**, 16206-39-6; **5e**, 16206-40-9; **5f**, 16206-41-0; **5g**, 16206-42-1; **6**, 16206-43-2; **7a**, 15561-15-6; **7a** (2,4-dinitrophenylhydrazone), 15561-16-7; **7b**, 94-41-7; 2,2′,5′-trimethylacrylophenone (2,4-dinitrophenylhydrazone), 16205-95-1; 2,2′,5′-trimethylacrylophenone, 16205-96-2; **10**, 16205-97-3; **13**, 16205-98-4; lead dioxide, 10377-43-2.

Acknowledgments.—We are grateful to the National Science Foundation (GE-7552) and the American Petroleum Institute for partial support of this research. We wish to thank Dr. O. C. Dermer for reading the manuscript, Dr. P. W. K. Flanagan for nmr spectra, and Mr. Mynard Hamming for mass spectra. This work was also partially supported by a NSF Academic Year Extension grant (GY-549) to D. V. H. and Panhandle State College, Goodwell, Okla.

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