was dissolved in benzene and chromatographed on a 40-cm. Florisil column; elution with benzene led to the isolation of VII (25%), III (26%), and a brown oil which was shown to contain unchanged IVb. The organic layer from a similar reaction was examined by quantitative g.l.c.[18] and no peaks corresponding to either IIb or phenyl cyclopropyl ketone (IX) were observed; an unidentified peak with a retention time of 22 min. was the only peak observed. Under the conditions employed, authentic samples of IIb and IX had retention times of 48 and 27 min., respectively.

When this reaction was carried out with phenyllithium as base, but under otherwise identical conditions, the only materials isolated were biphenyl and unchanged IVb.

Reaction of (2-Benzoylethyl)triphenylphosphonium Bromide (IVa) with *n*-Butyllithium.—The reaction of IVa (0.011 mole) and *n*-butyllithium (0.015 mole) was carried out in the same manner as in the preceding experiment. Chromatographic separation on a Florisil column led to the isolation of VII (50%) by elution with benzene and III (40%) and IVa (5%) by elution with acetone.

(2-Benzoyl-1-phenylethyl)triphenylphosphonium Bromide (XIII).—A mixture of 60 g. (0.208 mole) of β-bromo-β-phenylpropiophenone, prepared by the method of Kashiwagi,[19] 54.4 g. (0.208 mole) of triphenylphosphine, and 200 ml. of anhydrous benzene was refluxed for 3 hr. On cooling two layers formed; the viscous orange layer was heated on a steam bath with 200 ml. of acetone. XIII (87 g., 76%) was obtained when the solution was cooled; XIII was recrystallized from acetone and melted at 149.5–151.0°.

Anal. Calcd. for $C_{33}H_{28}BrOP$: C, 71.86; H, 5.12. Found: C, 71.42, 71.61; H, 5.39, 5.24.

The infrared absorption spectrum of XIII had bands at 1678 m, 1600 w, 1449 w, 1437 ms, 1325 w, 1212 ms, 1190 w, 1106 s, 996 w, 976 w, 917 w, 750 s, 727 s, 702 ms, and 690 ms cm.$^{-1}$.

Reaction of (2-Benzoyl-1-phenylethyl)triphenylphosphonium Bromide (XIII) with Phenyllithium.—A mixture of 11.0 g. (0.02 mole) of XIII, 0.025 mole of phenyllithium, and 1.3 l. of anhydrous toluene was refluxed for 24 hr., cooled, and concentrated under reduced pressure to a volume of 15 ml. The residue was chromatographed on a 60-cm. neutral alumina column; elution with petroleum ether gave 2.78 g. (53%) of VII and elution with ethyl acetate gave 2.00 g. (48%) of chalcone (XIV). No other materials could be isolated from the column. The infrared spectrum of the residue indicated the presence of XIII, but gave no indication of III. XIV was identified by mixture melting point and infrared spectra comparisons with an authentic sample.

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[18] Gas-liquid chromatography was carried out on an F and M Model 500 gas chromatograph using a 21-ft. Apiezon L column (16.9% on Chromosorb W, 110-120 mesh) at a column temperature of 200°, an injection port temperature of 245°, and a flow rate of 24.3 ml./min. (helium).

[19] H. Kashiwagi, *Bull. Soc. Chem. Japan*, **26**, 355 (1953).

The Preparation of Olefins by Pyrolysis of Carbalkoxyphosphonium Salts[1,2]

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It has been found that phosphonium salts, $R_3P^+CH_2CO_2R'X^-$, decompose at convenient rates at temperatures between 130 and 225°. The products of these decompositions are carbon dioxide, $R_3P^+CH_3\ X^-$, and an olefin derived from R′. Salts have been prepared and decomposed where R′ is a primary, secondary, or tertiary alkyl group. In most cases it was possible to isolate pure terminal olefins from decomposition of salts, R′ = 1°. Where isomer formation was possible, *i.e.*, R′ = 2°, 3°, the ratio of isomers was determined in many cases. A definite tendency to form the thermodynamically most stable olefins was noted. Olefins from several systems were found to be those arising from carbonium ion rearrangements.

Because of the general availability of alcohols, methods for their conversion to olefins have been the subject of constant investigation. In particular, mild methods have been sought. Pyrolytic decomposition of esters and xanthates has often been used.[5]

It is the purpose of this report to present a new and synthetically useful pyrolytic method for the conversion of an alcohol to an olefin. This work received its stimulus from the casual observations of Michaelis and Gimborn[6a] and Piaux.[6b] Michaelis and Gimborn found that triphenylcarbethoxymethylphosphonium chloride (I) slowly decomposes on heating at 100° to give triphenylmethylphosphonium chloride. They speculated, and quite reasonably so, that ethylene and carbon dioxide were the other products. Piaux found that

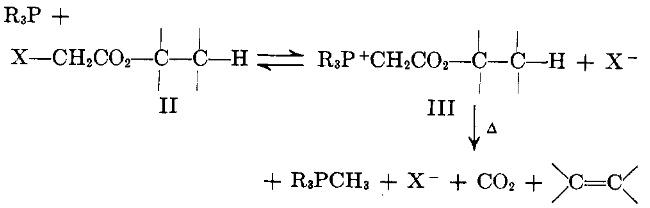
$$(C_6H_5)_3P^+CH_2CO_2C_2H_5 + \underset{I^-}{Cl^-} \longrightarrow (C_6H_5)_3P^+CH_3 + Cl^-$$

heating phenyldimethylcarbethoxymethylammonium iodide yielded phenyltrimethylammonium iodide.

The initial phase of this investigation was directed at establishing the course of decomposition of salts of this type. Having found that olefins were formed, the later work has been directed towards extending the reaction to systems which would establish its generality and limitations. The results of these experiments are now being reported.[7] Consideration of mechanism and related matters, in particular the solvolysis of these salts, will be discussed in a subsequent report.

Results and Discussion

It has been found that a wide variety of α-halo esters (II)[8] react with tributyl or triphenylphosphine to give salts (III). Heating of these salts at temperatures between 130 and 225° leads to decomposition with



$$R_3P + X{-}CH_2CO_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \rightleftharpoons R_3P^+CH_2CO_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H + X^- \xrightarrow{\Delta} R_3PCH_3 + X^- + CO_2 + {>}C{=}C{<}$$

R = C_4H_9, C_6H_5; X = Br, Cl

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[1] Research supported by the National Science Foundation.

[2] A preliminary account appeared in *J. Am. Chem. Soc.*, **83**, 3336 (1961).

[3] Rutgers Research Council Faculty Fellow, 1963-1964.

[4] National Science Foundation Cooperative Graduate Fellow in Chemistry, 1960-1961.

[5] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[6] (a) A. Michaelis and V. Gimborn, *Ber.*, **27**, 272 (1894); (b) L. Piaux, *Compt. rend.*, **190**, 645 (1930).

[7] For some interesting olefin-forming pyrolytic decompositions of phosphorus-containing compounds, see H. E. Baumgarten and R. E. Allen, *J. Org. Chem.*, **26**, 1533 (1961); W. J. Bailey, W. M. Muir, and F. Marktscheffel, *ibid.*, **28**, 2150 (1963).

[8] In general, α-bromoacetates were used. These were prepared in high yield by esterification with α-bromoacetic acid or, in the case of acid-sensitive alcohols, α-bromoacetyl bromide was used.

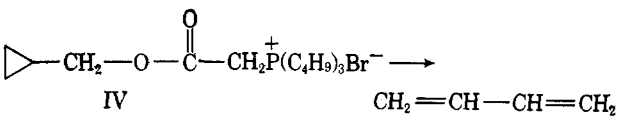
the production of carbon dioxide, a phosphonium halide, and an olefin derived from the alkoxy group of the salt (III).[9,10] It has been found that in general it is not necessary to isolate and purify the salts before pyrolysis. Indeed, the simplest and most generally applicable procedure developed involves mixing of the ester and tributylphosphine with cooling followed by heating at the appropriate temperature.

Decomposition of Primary Salts.—The salt from *n*-octyl bromoacetate and tributylphosphine was heated at 170° (bath) for 4 hr. to give a 72% yield of a mixture of octenes which was shown to consist of 60% 1-octene and 40% isomers. Repetition of this experiment at 110 mm., conditions under which the olefin was removed as formed, yielded 1-octene which was at least 96% pure.

Decomposition of the salt from tributylphosphine and *n*-butyl bromoacetate at 165° gave a mixture of butenes, 96% 1-butene, 3% *trans*-2-butene, and 1% *cis*-2-butene. Repetition of the experiment at 195° yielded 1-butene contaminated with *ca.* 1% of the isomeric 2-butenes. The total yields of olefins were not determined accurately but appeared to be excellent (*ca.* 90%).

Pyrolysis of the salt from tributylphosphine and 2-phenylpropyl bromoacetate at 210° yielded 74% of α-methylstyrene. Rearranged olefin, propenylbenzene, was not found in the product.

Decomposition of the cyclopropylcarbinyl salt (IV) at 155 and 200° yielded butadiene. It is not known whether methylenecyclopropane was formed and then isomerized to butadiene or whether rearrangement was synchronous with decomposition of IV.



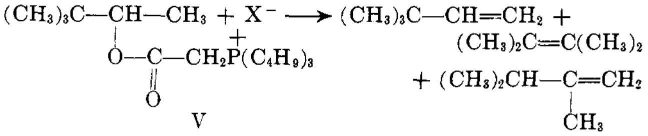
Decomposition of the *n*-decyl salt at 190° yielded 67% of mixed decenes. The composition of the olefin mixture was not determined nor was the reaction conducted under reduced pressure.[11]

The results of these experiments indicate that decomposition of primary salts has considerable merit as a means of introducing a terminal double bond. It is clear, though, that isomerization can occur if the olefin is not removed from the reaction mixture rapidly. There is some indication (cyclopropylcarbinyl system) that this may not always be possible.

Decomposition of Secondary Salts.—Decomposition of the 2-octyl salt at 190° yielded 76% mixed octenes, 2-heptyl at 280° yielded 76% mixed heptenes, and 1,2-diphenylethyl at 145° gave 90% *trans*-stilbene.

Pyrolysis of the salt from tributylphosphine and *sec*-butyl bromoacetate gave at 158 and 170° a mixture of butenes, whose composition varied little with the difference in pyrolysis temperature. The mixture consisted of 33% 1-butene, 48% *trans*-2-butene, and 19% *cis*-2-butene. The yields were excellent.

Both the chloride and bromide salts (V) were prepared and decomposed under a variety of conditions. In all cases, rearranged olefins, tetramethylethylene



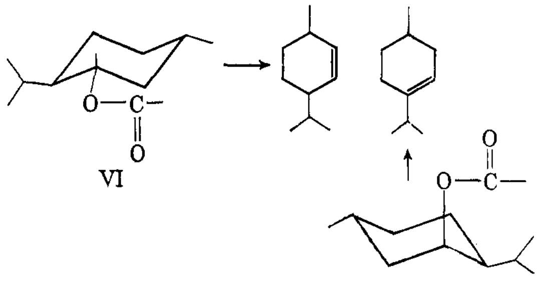
$$(CH_3)_3C\text{—}\underset{\substack{|\\ O\text{—}\underset{\substack{\|\\ O}}{C}\text{—}CH_2\overset{+}{P}(C_4H_9)_3}}{CH}\text{—}CH_3 + X^- \longrightarrow (CH_3)_3C\text{—}CH{=}CH_2 + (CH_3)_2C{=}C(CH_3)_2 + (CH_3)_2CH\text{—}\underset{\substack{|\\ CH_3}}{C}{=}CH_2$$

V

and 2,3-dimethyl-1-butene, were formed. The total yields were high. Pyrolysis of the bromide at 210° gave 92% of crude product which consisted of 82% of *t*-butylethylene, 11% tetramethylethylene, and 7% 2,3-dimethyl-1-butene. Other experiments gave good yields of mixed olefins but the per cent of unrearranged olefin was less than that obtained above.

The results of these experiments with secondary systems demonstrate that olefins can be obtained without difficulty; however, the possibility of skeletal rearrangement, presumably by a carbonium ion mechanism, detracts from its general application. In this sense acetate pyrolysis is considerably more specific; for example, the *t*-butylmethylcarbinyl system yields only *t*-butylethylene.[5] The mixture of isomers obtained from the *sec*-butyl system differs considerably from those found from acetate and xanthate pyrolyses and is considerably closer to the thermodynamic equilibrium mixture.[5]

Decomposition of Secondary Cycloalkyl Salts.—Decomposition of the cyclohexyl salt yielded 57% cyclohexene.[12] Decomposition of the *l*-menthyl (VI) and *d*-neomenthyl (VII) salts under a variety of conditions yielded a mixture of 2- and 3-menthenes. The 3-menthene invariably constituted at least 90% of the mixture. In one attempt to decompose VI at 120° (0.01 mm.), the components, *i.e.*, ester and phosphine, distilled, thus demonstrating the reversibility of salt formation.



VII

The salts from *cis*- and *trans*-2-phenylcyclohexanol were decomposed at 195° (*ca.* 0.5 mm.). The *trans* isomer yielded a mixture of 65% 1- and 35% 3-phenylcyclohexene while the *cis* led to 83% 1- and 17% 3-phenylcyclohexene. In a control experiment, 3-phenyl-

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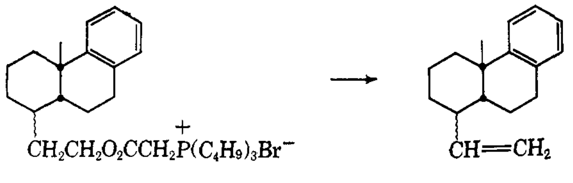
(9) For ease of discussion, salts derived from esters whose alkyl moiety is primary will be called primary salts, secondary salts, etc.

(10) Detailed descriptions of all of the experiments are available in the dissertations of C. J. R. and J. J. V., Rutgers, The State University, 1962. These theses are available on microfilm from University Microfilms, Ann Arbor, Mich.

(11) Recently Professor R. A. Barnes and E. P. Lira have pyrolyzed both diastereoisomeric salts illustrated under vacuum at 220°. Decomposition occurred in *ca.* 3 min. with the production of the terminal olefins in 80-90% yield.

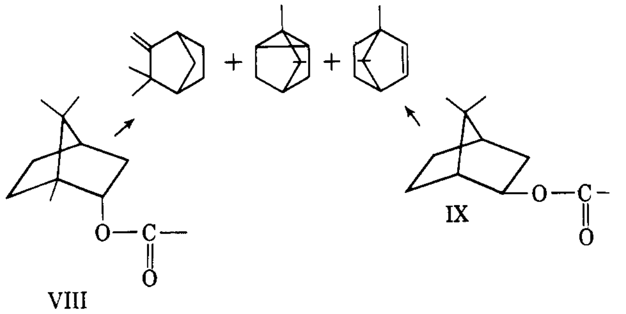


(12) Low yields are thought to be due mainly to mechanical losses and the relatively small amount of material decomposed in some cases.

cyclohexene was added to a reaction mixture and heated under reflux (180°) for 1 hr. The recovered olefin was essentially pure 3-phenylcyclohexene.

The results of these experiments and those in the menthyl series indicate that decomposition of the *d*-neomenthyl and *cis*-2-phenylcyclohexyl salts is not occurring by a *cis* elimination mechanism such as is proposed for the decompositions of acetates and xanthates.[5,13]

Decomposition of the bornyl (VIII) and isobornyl (IX) chlorides and bromides at 200° at atmospheric pressure and 100 mm. led to mixtures of camphene, tricyclene, and bornylene. In general, only traces of bornylene were formed; however, with the bornyl salts at 100 mm., 4–7% bornylene was formed. Camphene constituted 82–87% of the product and tricyclene 13–18%.



Decomposition of Tertiary Salts.—Little work was done with tertiary systems. It was found that the salt from *t*-amyl chloroacetate and tributylphosphine decomposed at 136° to give 60% mixed olefins, 32% 2-methyl-1-butene, and 68% 2-methyl-2-butene. It is interesting to note that this ratio of isomers is entirely different from that found by acetate pyrolysis, 76% 2-methyl-1-butene and 24% 2-methyl-2-butene.[5]

Experimental[14]

Materials.—Tributylphosphine was obtained from FMC Co. It was fractionated, b.p. 124° (21 mm.), and stored in a serum-capped bottle under nitrogen. Triphenylphosphine was obtained from M & T Chemical Company. It was recrystallized from ethanol before use and had m.p. 81–82°. The alcohols used to prepare the esters were either available commercially or were synthesized by methods reported in the literature. In all cases their properties agreed well with those reported. Conventional esterification techniques proved satisfactory for the preparation of most α-halo esters. With tertiary and acid-sensitive alcohols the α-halo acid halide and pyridine were used. Most new α-halo esters were analyzed and gave satisfactory analytical results. In some cases where only small quantities of alcohol were available this was not done. The infrared spectra of all the esters were in agreement with the assigned structures.

Olefin Analysis.—The ratio of isomers of the olefins obtained from the pyrolyses was determined by g.l.p.c. except for the phenylcyclohexenes where ultraviolet measurements were employed. The identification of the various isomers by g.l.p.c. was conducted in the main by comparing retention times with those of known samples. These materials were either available commercially or were prepared by known methods. The per cent of each isomer present in the pyrolysates was determined by measuring and averaging the area under the curves obtained from three or more chromatograms. In all cases it was assumed that the thermal conductivities of the isomers were the same.

Decompositions.—The salts were formed at the outset of this work by reaction with triphenylphosphine. These materials were usually crystalline and easily purified. Most of the later work involved *in situ* formation of the salt by the cautious addition with cooling and stirring of tri-*n*-butylphosphine to the α-halo ester. A one-piece distillation head was attached and the salt was pyrolyzed by immersing the flask in a Wood's metal bath at the appropriate temperature. In cases of small quantities of salt the decompositions were often conducted in a molecular still. Several representative decompositions are described below.

The salt from *sec*-butyl bromoacetate, 19.0 g. (0.10 mole), and tributylphosphine, 20.2 g. (0.01 mole), was pyrolyzed at 170°. The distillate was collected in a Dry Ice-cooled receiver. After 4 hr. distillation ceased. The mixture of butenes was analyzed by g.l.p.c. with a 2,5-hexanedione column at room temperature.

2-Phenylpropyl bromoacetate (5.0 g., 0.0201 mole) was allowed to react with 4.1 g. (0.0201 mole) of tributylphosphine. The salt was heated for 1 hr. at 210° (bath). No distillate was observed. The pressure was lowered to 20 mm. and 2.0 g. (74%) of material distilled. The infrared spectrum showed no trace of alcohol or ester and it was identical with that of α-methylstyrene. G.l.p.c. analysis confirmed the infrared analysis. With a 2-ft. silicone gum rubber column at 70° α-methylstyrene had a retention time of 4.0 min. and propenylbenzene 5.8 min. Only α-methylstyrene was found in the distillate.

The salt from 5.0 g. (0.0216 mole) of bornyl chloroacetate and 4.3 g. (0.0216 mole) of tributylphosphine was pyrolyzed in a molecular still at 200° (block) and 100 mm. After 4 hr., 2.1 g. (68%) of material was collected. The infrared spectrum of the product, when compared to that of an authentic sample of commercial camphene, showed it to be mainly camphene. The spectrum had a peak at 717 cm.$^{-1}$ which was not present in the commercial camphene. This band has been ascribed to bornylene.[15] G.l.p.c. analysis indicated three components with retention times of 5.0, 5.4, and 6.8 min. on a 15-ft. Carbowax column at 155°. The later two components appear in commercial camphene in the ratio 1:10. It was on this basis that the 5.4-min. component was assigned to tricyclene and the 6.4-min. component to camphene.

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(13) This conclusion depends on there being little isomerization of the least-substituted olefin under the conditions of the experiment. The control experiment supports this.

(14) Analyses were by G. Robertson, Florham Park, N. J. The infrared spectra were obtained with Perkin-Elmer Model 21 or 137 instruments. Ultraviolet spectra were obtained with a Cary Model 11MS. Melting points and boiling points are uncorrected.

(15) J. McKenna and J. B. Slinger, *J. Org. Chem.*, **23**, 2759 (1958).