combustion was preferred.[19] Carbon dioxide from barium carbonate was liberated by hot sulfuric acid.

The radioactivity assay was performed in a 250-ml. DC type 302 stainless steel ionization chamber connected to a vibrating reed Dynacon Electrometer model 600, made by Nuclear-Chicago Corporation. It was equipped with a 10 millivolt G-11 strip-chart recorder, made by Varian Associates, Palo Alto, Calif. Each sample was assayed both by the steady state and by the rate of charge methods. At least two assays were made from each sample. Accuracies of the measurements were within ±0.5–1% for barium carbonate samples, ±1–2% for benzoic and isophthalic acids and ±2.5–5% for benzene samples. This variation is within the accuracy limit of the instrument as indicated by the manufacturer except for benzene. The very small radioactivities of the benzene samples were sometimes only ten times as much as the background current.

Radioactivity of Carbonaceous Material.—The carbonaceous material was burned off from the catalyst with an air–nitrogen mixture as described previously.[7] Carbon dioxide was absorbed in 500 ml. of carbon dioxide-free dilute sodium hydroxide solution; 260 ml. of this solution yielded 0.4785 g. of barium carbonate precipitate, which corresponds to 4.66 mmoles of carbon dioxide for the entire carbonaceous material. 2,2,3-Trimethylpentane (50.4 mmoles, with a specific radioactivity of 7.5 μc./millimole) was passed through the catalyst; 4.66 millimoles of CO_2 correspond to 4.66/8 = 0.582 mmoles of C_8H_{18}, or 1.15% of the total hydrocarbon feed. The radioactivity of the barium carbonate was 0.9 μc./mmole, which is only slightly less than that of the feed, which was 7.5 μc./mmole C_8H_{18}, or 0.94 μc./milli-atom C.

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[19] H. Pines and A. W. Shaw, *J. Am. Chem. Soc.*, **79**, 1474 (1957).

[Contribution from The School of Chemistry, Rutgers, The State University, New Brunswick, N. J.]

A New Synthesis of Cyclopropanecarboxylic Acids[1,2]

By Donald B. Denney, John J. Vill[3] and Marvin J. Boskin

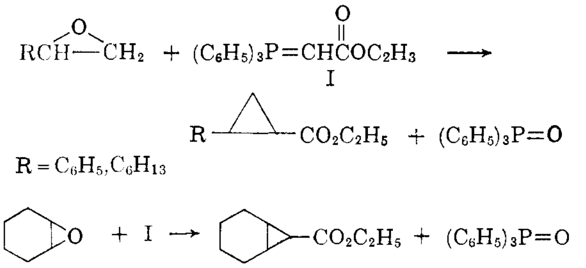
Received May 3, 1962

Carbethoxymethylenetriphenylphosphorane (I) reacts with cyclohexene oxide, 1-octene oxide and styrene oxide to give ethyl norcaranecarboxylate, ethyl *trans*-2-hexylcyclopropanecarboxylate and ethyl *trans*-2-phenylcyclopropanecarboxylate. The yields in these reactions are in the range 30–60%. Optically active styrene oxide and I gave optically active ethyl *trans*-2-phenylcyclopropanecarboxylate. Some mechanistic features of these reactions are discussed.

In recent years the use of phosphoranes as synthetic tools has become increasingly important.[4] This report describes the preparation of substituted cyclopropanecarboxylic esters from carbethoxymethylenetriphenylphosphorane (I) and epoxides.

Results

Heating a mixture of I and 1-octene oxide at 200° for eight hours gave a 46% yield of ethyl *trans*-2-hexylcyclopropanecarboxylate. These conditions were determined as being optimal for these particular reactants by conducting a series of experiments at different temperatures. Gas–liquid chromatographic analysis of aliquots withdrawn at suitable time intervals indicated that the above conditions led to the highest yields.

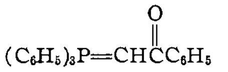


Several potential catalysts for the reaction of I and 1-octene oxide were investigated. It was found that hydroquinone and aluminum isopropoxide had minor catalytic activity. Boron trifluoride etherate inhibited the reaction and triamyl borate had little effect.

Attempts to conduct the reaction of I and 1-octene oxide in dimethylformamide, diethylene glycol dimethyl ether and nitrobenzene were unsuccessful.

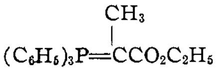
Reaction of I with cyclohexene oxide at 200° (bath) gave a 56% yield of ethyl norcaranecarboxylate. Similarly *dl*-styrene oxide and I gave a 30% yield of ethyl *trans*-2-phenylcyclopropanecarboxylate. In another run, direct conversion to the acid and re-esterification gave a 38% yield. *l*-Styrene oxide and I gave, *via* the acid and then esterification, methyl *l*-*trans*-2-phenylcyclopropanecarboxylate.

Several attempts to use other phosphoranes, II and III, in this reaction were unsuccessful. Triphenylbenzoylmethylenephosphorane (II) did not react with 1-octene oxide. Some reaction did occur between III and 1-octene oxide as was evidenced by the obtention of >90% yields of triphenylphosphine oxide. The other products appeared to be polymeric and were not characterized.



$(C_6H_5)_3P{=}CH\overset{O}{\overset{\|}{C}}C_6H_5$

II



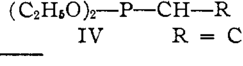
$(C_6H_5)_3P{=}\overset{CH_3}{\overset{|}{C}}CO_2C_2H_5$

III

In another series of experiments, compound I was allowed to react with 1-butene episulfide at reflux, in chloroform at reflux and at room temperature. In each case only unreacted phosphorane and polymeric material was obtained.

Discussion

Although the reaction conditions required for this synthesis are vigorous, relatively good yields of the desired cyclopropane-containing compounds have been obtained. Recently Wadsworth and Emmons[5] have shown that phosphonate carbanions IV react with epoxides to give substituted cyclopropanes. The carbanions IV are considerably



$(C_2H_5O)_2\text{—}\overset{O}{\overset{\uparrow}{P}}\text{—}\overset{\ominus}{C}H\text{—}R$

IV R = $CO_2C_2H_5$, CN

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(1) Supported by the National Science Foundation.

(2) A preliminary account appeared in *J. Am. Chem. Soc.*, **81**, 6330 (1959).

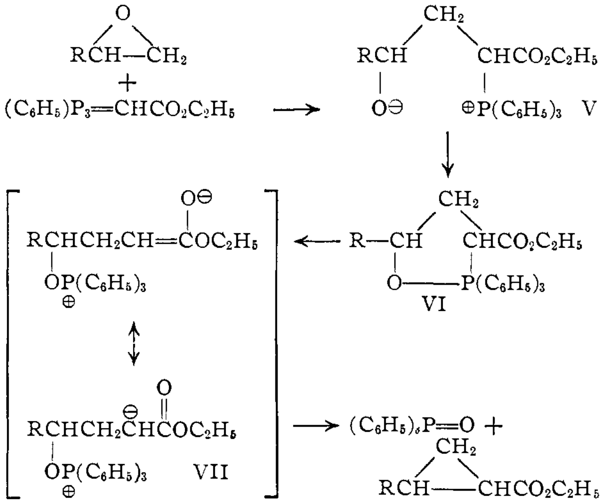
(3) National Science Foundation Coöperative Graduate Fellow, 1960–1961.

(4) U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

(5) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

more reactive than I and allow the syntheses to be carried out at considerably lower temperatures than those required for I and epoxides.[6] The phosphonate carbanions are somewhat more difficult to prepare than compound I and must be used immediately. Because of these factors it appears that both methods have their place in organic synthesis.

The mechanism of these reactions is of considerable interest. It was suggested[2] that the initial reaction involves nucleophilic displacement by I on the epoxide to give an intermediate, V, which can ring close to VI. Subsequent ring opening gives VII which collapses to products by an intramolecular SN2 process. Several pieces of evidence support this proposal. The finding that optically active styrene oxide yields optically active ethyl *trans*-2-phenylcyclopropanecarboxylate is of particular importance. The proposed mechanism predicts retention of optical activity in the product. It also suggests that inversion of configuration should occur. Unfortunately the absolute configurations of the optical isomers of *trans*-2-phenylcyclopropanecarboxylic acid are not known[7]; therefore it is not possible to state whether the reaction proceeds with inversion or retention of configuration.



The fact that cyclohexene oxide yields a cyclopropanecarboxylate is in harmony with the proposed mechanism and argues in favor of inversion in the final ring closure. Recently McEwen and Wolf[8a] and McEwen, Bladé-Font and VanderWerf[8b] have provided evidence which favors the proposed mechanism.

The mechanism explains the observation that II does not react with epoxides under the conditions employed. This undoubtedly is due to the lower nucleophilicity of II as compared to I. It is interesting to note that if the initial reaction of II with an epoxide could be effected the subsequent reactions should be particularly facile.

Experimental[9]

Reaction of I and 1-Octene Oxide.—A mixture of 17.6 g. (0.051 mole) of I and 19.5 g. (0.152 mole) of 1-octene oxide was heated under reflux, bath temperature 200°, for 8 hours. The mixture was fractionated to yield ethyl *trans*-2-hexylcyclopropanecarboxylate, b.p. 120° (10 mm.), 4.6 g. (46%). Gas–liquid chromatographic analysis on a 1.5-m. Carbowax column at 150° with a helium flow rate of 60 ml./min. gave only one peak with a retention time of 10 min. The infrared spectrum was essentially identical with that of the ester prepared by the diazoacetic ester synthesis.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.72; H, 11.11. Found: C, 72.75; H, 11.05.

In another experiment the crude reaction product was saponified and the crude acid was converted to the *p*-bromophenacyl ester which after crystallization from aqueous ethanol had m.p. 90–91° (lit.[10] 90.5–91° for the *trans-ester*). The yield was 51%.

Process Study of the Reaction of I and 1-Octene Oxide.—Mixtures of 5.0 g. (0.015 mole) of I and 5.0 g. (0.04 mole) of 1-octene oxide were heated at bath temperatures of 150, 175, 200 and 225°. Aliquots were removed at 2, 4, 6, 8, 24, 48 and 72 hours. Gas-liquid chromatographic analysis indicated that at 200° and after 8 hours, the maximum yield of ethyl *trans*-2-hexylcyclopropanecarboxylate had been obtained. Further heating led to degradation of the ester.

Effect of Additives on the Reaction of I and 1-Octene Oxide.—Mixtures of 5.0 g. (0.015 mole) of I and 5.0 g. (0.04 mole) of 1-octene oxide were heated at 190° in the presence of 10 mole % of hydroquinone, boron trifluoride etherate, triamyl borate and aluminum isopropoxide. Aliquots were removed from each reaction mixture at 2, 4, 6 and 8 hours; G.L.C. analysis indicated that hydroquinone and aluminum isopropoxide shortened the reaction time from 8 hours to *ca.* 2 hours. No improvement in yield was found and after 8 hours the uncatalyzed reaction showed the highest percentage of product.

Preparation of Ethyl 2-Hexylcyclopropanecarboxylate from 1-Octene and Methyl Diazoacetate.—Reaction of methyl diazoacetate and 1-octene[10] gave a mixture of methyl esters which was saponified. The crude acid mixture was esterified with ethanol and distilled, b.p. 130° (19 mm.) (lit.[10] 75–80°, 0.05 mm.); G.L.C. analysis gave two peaks, whose areas were in the ratio 4:1. The retention times were 10 and 14 min., respectively.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.72; H, 11.11. Found: C, 72.80; H, 11.20.

Reaction of I and Cyclohexene Oxide.—A mixture of 5.0 g. (0.015 mole) of I and 10 g. (0.12 mole) of cyclohexene oxide were heated at 200° (bath) for 8 hours. The mixture was diluted with 50 ml. of methanol, and 15 ml. of 6 *N* potassium hydroxide was added. The solution was heated under reflux for 12 hours, then poured into 100 ml. of water and extracted with 100 ml. of chloroform. The aqueous solution was acidified with concentrated hydrochloric acid and extracted with two 50-ml. portions of ether. The ether extract was dried over sodium sulfate and the ether was evaporated. One crystallization from aqueous methanol gave 1.5 g. (63%) of 7-norcaranecarboxylic acid, m.p. 87–89° (lit.[11] 97–98°). A small sample was sublimed at 90° (block) and 25 mm. to give needles, m.p. 97–98°.

The acid, m.p. 87–89°, 1.0 g., was boiled with 5 ml. of thionyl chloride for 30 min. The mixture was poured into ice-cold ammonium hydroxide. The precipitate was washed with water and crystallized from dilute ethanol to give 0.5 g. of 7-norcaranecarboxamide, m.p. 224–225° (lit.[11] 225–226°).

A mixture of 10.0 g. (0.028 mole) of I and 10.0 g. (0.102 mole) of cyclohexene oxide was heated at 200° (bath) for 26 hours. The reaction mixture was distilled to give 2.6 g. (56%) of ethyl 7-norcaranecarboxylate, b.p. 80–82° (1 mm.), (lit.[11] 110°, 18 mm.).

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[6] Recent work in this Laboratory indicates that $(C_4H_9)_3P{=}CHCO_2C_2H_5$ is considerably more reactive than compound I and reacts with epoxides in refluxing benzene to give cyclopropanecarboxylates.

[7] Prof. H. M. Walborsky has informed us that this determination is currently under investigation in his laboratory.

[8] (a) W. E. McEwen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 676 (1962); (b) W. E. McEwen, A. Bladé-Font and C. A. VanderWerf, *ibid.*, **84**, 677 (1962).

[9] Analyses by G. Robertson, Florham Park, N. J. Melting points are uncorrected.

[10] K. Hofmann, O. Tucker, W. R. Miller, A. C. Young, Jr., and F. Tausig, *J. Am. Chem. Soc.*, **76**, 1799 (1954).

[11] M. Mousseron, R. Jacquier and R. Fraisse, *Compt. rend.*, **243**, 1880 (1956).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.43; H, 9.57. Found: C, 71.50; H, 9.55.

Reaction of I and *dl*-Styrene Oxide.—A mixture of 12.0 g. (0.0345 mole) of I and 24.0 g. (0.20 mole) of styrene oxide was heated at 170° (bath) for 24 hours. The cooled reaction mixture was triturated with hexane. The solid residue was washed with hexane and dried *in vacuo* to give 8.5 g. (89%) of triphenylphosphine oxide, m.p. 155–157° (lit.[12] 153°). The hexane solution was concentrated and then fractionated to give 20.3 g. of recovered styrene oxide, b.p. 74° (12 mm.), and 2.0 g. (30%) of ethyl *trans*-2-phenylcyclopropanecarboxylate, b.p. 102° (0.15 mm.), (lit.[13] 105–110°, 2 mm.).

In another experiment, 12.0 g. (0.03 mole) of I and 12.0 g. (0.10 mole) of styrene oxide were heated at 190–200° (bath) for 6 hours. Following the procedure above, 90% of triphenylphosphine oxide, m.p. 156–158°, was obtained. The infrared spectrum was identical to that of an authentic sample.

Distillation afforded, after removal of hexane and styrene oxide, 1.2 g. (21%) of ethyl *trans*-2-phenylcyclopropanecarboxylate, b.p. 103–105° (0.5 mm.).

The ester from another run was converted to the acid by heating 1.90 g. (0.01 mole) with 15 ml. of 6 *N* potassium hydroxide and 6 ml. of methanol for 6 hours. Acidification gave the acid which was recrystallized twice from aqueous ethanol containing a little hydrochloric acid; m.p. 90–91° (lit.[13] 92–93°).

The amide was prepared by boiling 1.0 g. of the acid in 5 ml. of thionyl chloride for 20 minutes. The mixture was poured into 15 ml. of ice-cold concentrated ammonium hydroxide. The amide was recrystallized from aqueous methanol; m.p. 190.5–192° (lit.[13] 190–191°).

Reaction of I and *l*-Styrene Oxide.—A mixture of 10.0 g. (0.029 mole) of I and 10.0 g. (0.084 mole) of *l*-styrene oxide,[14] $[\alpha]^{20}D$ −12.45°, *c* 20 in chloroform, was heated at 200° (bath) for 7 hours. The cooled mixture was dissolved in 30 ml. of methanol and 15 ml. of 6 *N* potassium hydroxide was added. The mixture was boiled for 12 hours. Extraction with chloroform followed by acidification gave 10 g. of an amber semi-solid which was taken up in ether and esterified by adding a solution of diazomethane in ether. The resulting ester was molecularly distilled, b.p. 90° (block) (25 mm.), to give 1.5 g. (28%) of methyl *trans*-2-phenylcyclopropanecarboxylate, $[\alpha]^{20}D$ −31.3°, *c* 13 in chloroform.

The ester was saponified and the acid was converted to the amide, m.p. 192–193° (lit.[13] 190–191° for the *dl*-amide), $[\alpha]^{23}D$ +8.15°, *c* 2 in 95% ethanol.

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[12] G. M. Kosolapoff, "Organophosphorus Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1950, p. 114.

[13] A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).

[14] Prepared according to the procedure of E. L. Eliel and D. W. Delmonte, *J. Org. Chem.*, **21**, 596 (1956).

[CONTRIBUTION FROM EMERYVILLE RESEARCH CENTER, SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

Oxidation of Free Radicals from Unsaturated Compounds by Cupric Salts

BY JAY K. KOCHI[1] AND FREDERICK F. RUST

RECEIVED APRIL 23, 1962

Cupric salts react with alkyl radicals by two oxidation–reduction processes which have been described as electron transfer and ligand transfer. We have studied the oxidation of substituted alkyl radicals by examining the competitive rates of oxidation of 5-(methoxycarbonyl)-pentyl and the radicals resulting from its addition to a variety of monomers. By regulating the concentration of monomer and cupric salt, it is possible to oxidize selectively allylic radicals in the presence of the primary hexanoate ester radicals. 5-(Methoxycarbonyl)-pentyl reacts with butadiene in methanol under these conditions to produce methyl methoxydecenoates. Isoprene, chloroprene, styrene and acrylonitrile are also effective radical acceptors. The mechanism of the oxidation of substituted alkyl radicals by cupric salts is discussed.

Introduction

The oxidation of relatively simple free alkyl radicals by cupric salts was previously described[2] as involving either a ligand transfer process or an electron transfer process depending on the particular cupric salt employed. Part of the problem encountered in describing these reactions in a more quantitative manner is the difficulty in obtaining meaningful rate data. Competitive experiments based on product isolation at present forms the basis of obtaining some semi-quantitative kinetic information. In this paper we wish to present studies on the competitive oxidation of substituted carbon free radicals by examining the products from the oxidation by cupric salts of 5-(methoxycarbonyl)-pentyl (I) in the presence of unsaturated compounds. The competitive reactions are (a) the oxidation of the 5-(methoxycarbonyl)-pentyl, (b) the addition to an unsaturated compound and (c) the oxidation of the resulting adduct radical. 5-(Methoxycarbonyl)-pentyl was chosen because of the relative ease of isolation of its oxidation products.

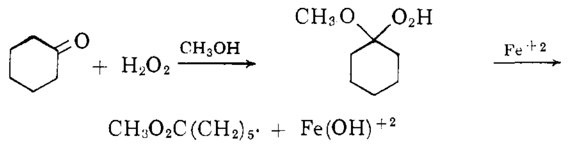
$$\underset{\text{I}}{CH_3O_2C(CH_2)_5\cdot} + Cu^{II}X_n \xrightarrow{a} \text{oxidation products} + Cu^{I}X_m$$

$$CH_3O_2C(CH_2)_5\cdot + CH_2{=}CHX \xrightarrow{b} CH_3O_2C(CH_2)_6\dot{C}HX$$

$$CH_3O_2C(CH_2)_6\dot{C}HX + Cu^{II}X_n \xrightarrow{c} \text{oxidation products} + Cu^{I}X_m$$

Results

Cyclohexanone and hydrogen peroxide react to form a complex mixture of adducts.[3] In methanol this mixture reacts with ferrous sulfate to produce the radical 5-(methoxycarbonyl)-pentyl.



This radical will react with a variety of unsaturates.[4] In the case of butadiene, for example, 5-(methoxycarbonyl)-pentyl adds to produce an

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[1] Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio.

[2] H. E. De La Mare, J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 2013 (1961); to be published; J. K. Kochi, *ibid.*, **84**, 774, 1572, 1192, 2121, 2785 (1962); *Tetrahedron*, **18**, 483 (1962).

[3] M. S. Kharasch and G. Sosnovsky, *J. Org. Chem.*, **23**, 1322 (1958).

[4] M. S. Kharasch and W. Nudenberg, *ibid.*, **19**, 1921 (1954). D. D. Coffman and H. N. Cripps, U. S. Patent 2,811,551 (to du Pont), Oct. 29, 1957.