Preparation of 3-Methyl-3-phenyl-2-butanone.—Six grams of magnesium metal turnings washed with a solution of iodine and ethyl ether was placed in a 500-ml. three-necked round-bottomed flask containing a Dry Ice condenser, stirrer, and gas inlet tube. One hundred milliliters of anhydrous ethyl ether was added and methyl bromide (b.p. 4.5°) was bubbled into the ether. The reaction started after adding a crystal of iodine and warming the ether. All the magnesium was dissolved after 2 hr. The Dry Ice condenser was replaced with a water-cooled condenser and 49 g. of cadmium chloride, previously dried to constant weight, was added. The slurry was refluxed for 50 min. until the solution gave a negative Gilman test. The ether was evaporated under nitrogen and 100 ml. of anhydrous benzene was added. With good stirring a solution of 25.7 g. (0.068 mole) of α-phenylisobutyryl chloride in 100 ml. of anhydrous benzene was added to the benzene solution of methylcadmium chloride. The solution was refluxed for 4 hr., cooled, and acidified with 20% sulfuric acid and ice. The benzene layer was separated and washed with 10% hydrochloric acid, 10% sodium hydroxide and water. After drying with sodium sulfate, the benzene solution was evaporated, and the resulting oil (19.1 g., 84%) distilled at 97° (0.5 mm.) [lit.,[5] 97–98° (11 mm.)]; $\nu_{\max}^{\text{KBr}}$ 2985 (with shoulders; aliphatic and aromatic CH) and 1701 cm.$^{-1}$ (CO). A vapor phase chromatogram (F and M 500 programmed temperature gas chromatograph with Carbowax 20 M column) showed the ketone was over 99% pure.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.23; H, 8.55.

3-Methyl-3-phenyl-2-butylidenemalononitrile (IV).—Sixteen grams of 3-methyl-3-phenyl-2-butanone was dissolved in 150 ml. of anhydrous benzene and refluxed for 48 hr. with 8 g. of malononitrile, 3 g. of ammonium acetate, and 9 ml. of glacial acetic acid. Evaporation of the solvent gave an oil, which was distilled under reduced pressure. The first fraction collected (10.8 g.) was the starting ketone, b.p. 88–90° (0.2 mm.), and the second fraction, 5.2 g., b.p. 130–135° (0.25 mm.), had a peak in the infrared at 2220 cm.$^{-1}$. Redistillation gave an analytical sample collected at 133° (0.25 mm.).

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.67; N, 13.33. Found: C, 80.12; H, 7.03; N, 12.98.

Ring Closure of 1-Methyl-2-phenylisobutylidenemalononitrile (IV).—Two hundred milligrams of IV was allowed to react in 4 ml. of concentrated sulfuric acid at room temperature for 1 hr. A white solid precipitated after the dark green solution was poured into 40 g. of ice and allowed to stand overnight. Recrystallization from alcohol gave 152 mg. (78%) of white needles, m.p. 164–165°. The infrared spectrum was identical to IIIc and a mixture melting point showed no depression.

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Reaction of *t*-Butoxy Radical with 4-Vinylcyclohexene

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In continuation of a study of the reaction of free radicals with olefins, it became evident that further work was required to elucidate one phase of the work previously reported.[2]

The previous work had reported that the slow photolysis of di-*t*-butyl peroxide in 4-vinylcyclohexene yielded dehydrodimers and that the more rapid copper-induced decomposition resulted in both *t*-butyl vinylcyclohexenyl ethers and dehydrodimers. Reference was made to the work of Kharasch and Fono,[3] but it was also suggested that perhaps increased radical concentration resulting from more rapid peroxide decomposition might explain the production of the *t*-butyl vinylcyclohexenyl ether. Recent studies reported by Kochi[4] on the mechanism of the copper salt-catalyzed reactions of peroxides suggested the possibility of involvement of cupric *t*-butoxide in the reaction to form the ether provided the copper salt was sufficiently soluble in the reaction medium.

In order to test these two hypotheses, four reactions of di-*t*-butyl peroxide with 4-vinylcyclohexene were carried out at a temperature of 80°. These are written below in equation form with the major products indicated.

$$(t\text{-BuO})_2 + C_8H_{12} \xrightarrow[\text{heat}]{} t\text{-BuOH} + (C_8H_{11})_2 \qquad (1)$$

$$(t\text{-BuO})_2 + C_8H_{12} \xrightarrow[\text{heat}]{\text{CuCl}_2} t\text{-BuOH} + t\text{-BuO-}C_8H_{11} + (C_8H_{11})_2 \qquad (2)$$

$$(t\text{-BuO})_2 + C_8H_{12} \xrightarrow[\text{heat}]{h\nu} t\text{-BuOH} + (C_8H_{11})_2 \qquad (3)$$

$$(t\text{-BuO})_2 + C_8H_{12} \xrightarrow[\text{heat}]{h\nu,\text{CuCl}_2} t\text{-BuOH} + (C_8H_{11})_2 \qquad (4)$$

The rate of disappearance of di-*t*-butyl peroxide was observed to be the same in reactions 3 and 4 which was more rapid than 1 and 2. Comparison of 1 and 2 at 115° showed that reaction 2 is faster than 1. One also observes that reaction 2 in which the reactants are heated in the presence of copper salt is the only reaction to produce *t*-butyl vinylcyclohexenyl ether and that the photolysis reactions with or without cupric chloride produce no ether. In the case of reaction 2 the ether is formed in approximately the same amount as the dehydrodimer as determined by gas chromatography. One concludes from these data that the production of *t*-butyl vinylcyclohexenyl ether is definitely not a result of a radical concentration effect.

The formation of *t*-butyl vinylcyclohexenyl ether is visualized as occurring through a mechanism analogous to the one proposed by Kochi[4] in which a free radical R· is oxidized by a cupric salt, Cu(II)OX, to form ROX and Cu(I).

$$(t\text{-BuO})_2 + \text{Cu(I)} \longrightarrow t\text{-BuO}\cdot + t\text{-BuOCu(II)}$$

$$t\text{-BuO}\cdot + C_8H_{12} \longrightarrow t\text{-BuOH} + C_8H_{11}\cdot$$

$$t\text{-BuOCu(II)} + C_8H_{11}\cdot \longrightarrow t\text{-BuO-}C_8H_{11} + \text{Cu(I)}$$

$$2C_8H_{11}\cdot \longrightarrow (C_8H_{11})_2$$

Although cupric chloride was used in this study, some cuprous salt would soon be formed as a result of slow thermal decomposition of peroxide to produce free radicals which would initiate the above sequence. The production of dehydrodimer probably results from a coupling of vinylcyclohexenyl radicals.

Gas chromatography also indicated that a small amount of lower boiling materials was formed in the reactions. Infrared analysis was consistent with a product formed by attack of $CH_3\cdot$ radicals on 4-vinylcyclohexene. The spectra of two of the materials

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showed, in one case, no vinyl absorption but internal unsaturation and methyl absorption; the other material examined showed absorptions corresponding to a methyl group and both vinyl and internal unsaturation. The spectra were otherwise similar to that of 4-vinylcyclohexene. Thus both addition and substitution products are found. Acetone was also found to be produced in these reactions showing that some cleavage of *t*-butoxy radical to form $CH_3\cdot$ must also have occurred.

Experimental

Reagent.—Di-*t*-butyl peroxide (Shell) was distilled at reduced pressure before use. The 4-vinylcyclohexene (Cities Service) was passed through an activated alumina column immediately before use.

All experiments were performed in a 1-l., three-necked, round-bottom flask equipped with a quartz test tube in the center neck. A length of hypodermic tubing was inserted through a serum cap attached to one of the flask necks. Samples were removed by placing evacuated sample vials onto this tubing and withdrawing approximately 1 ml. of solution. The reactions were stirred at all times by a magnetic stirring bar.

4-Vinylcyclohexene (165 g., 1.5 moles) was heated in the flask described above, and di-*t*-butyl peroxide (36 g., 0.25 mole) was heated simultaneously under nitrogen in a dropping funnel attached to the flask. When both were at the desired temperature (80 or 115°) the peroxide was added. Samples were withdrawn at appropriate time intervals. In those reactions involving cupric chloride, 0.3 g. of cupric chloride (dihydrate) was added to the 4-vinylcyclohexene before heating. The photolysis reactions were performed using a G.E. H85A3/UV lamp inserted into the quartz test tube mentioned above.

t-Butyl peroxide concentration was measured by gas chromatography at 75° on a 6-ft. silicone gum rubber column. Product analysis was also carried out by gas chromatography on a 6-ft. Carbowax (20M) column, programming from 100–250°. Product identification was by infrared spectroscopy. The following absorptions were observed in the 4-vinylcyclohexenyl ethers: 3090 $cm.^{-1}$ vinyl unsaturation, 3030 $cm.^{-1}$ *cis*-internal unsaturation, the typical aliphatic C–H absorptions around 2900 $cm.^{-1}$, 1640 $cm.^{-1}$ vinyl unsaturation, 1390 $cm.^{-1}$ and 1360 $cm.^{-1}$ assigned to *t*-butyl, 1155 $cm.^{-1}$ typical of ethers, 997 $cm.^{-1}$ and 915 $cm.^{-1}$ vinyl unsaturation, and 690 $cm.^{-1}$ assigned to internal unsaturation. The dehydrodimers showed the following absorptions: 3080 $cm.^{-1}$ vinyl unsaturation, 3030 $cm.^{-1}$ *cis*-internal unsaturations, aliphatic C–H absorptions between 3000 and 2800 $cm.^{-1}$, 1640 $cm.^{-1}$ vinyl unsaturation, 997 and 910 $cm.^{-1}$ vinyl unsaturation, 660 $cm.^{-1}$ internal unsaturation. The over-all infrared spectrum of the dehydrodimer showed the presence of all the major absorptions of 4-vinylcyclohexene, the only marked exception being the moderately strong 4-vinylcyclohexene peak at 1140 $cm.^{-1}$ (unassigned) absent in the dehydrodimer.

Comparison with previous work,[2] in which both the ether and dehydrodimer were isolated and characterized by infrared, hydrogenation, and elemental analysis, further confirmed the identification.

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Dibenzyl Carbethoxy Phosphate

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Several anhydrides of phosphoric acid with carboxylic acids of the type $RCO-O-PO(OH)_2$ have been described,[1] in which R is a simple alkyl or aryl group. Much interest has been directed to the chemical and biological properties of acetyl phosphate.[2] No anhydride of phosphoric acid with a monoalkyl carbonic acid, in which R = alkoxy, has been described.

In the present work, dibenzyl carbethoxy phosphate was prepared by reaction of dibenzyl silver phosphate with ethyl chloroformate.

$$(C_7H_7O)_2POOAg + ClC(O)OC_2H_5 = (C_7H_7O)_2P(O)OC(O)OC_2H_5 + AgCl$$

The product is colorless oil, which is stable at 0°.

In aqueous dioxan (1:1 by volume), dibenzyl carbethoxy phosphate undergoes hydrolysis and dibenzyl hydrogen phosphate is formed. The progress of hydrolysis can be followed by neutralizing the acid as it is produced, using an automatic pH-stat titrator. The reaction observed first-order kinetics. At a constant pH of 6.0 and 37°, $k = (3.53 \pm 0.02) \times 10^{-5}$ $sec.^{-1}$, using initial concentrations of 2 to 9 mmoles of the anhydride.

Attempts were made to remove the benzyl groups and to obtain carbethoxy phosphate, $C_2H_5O\ C(O)\text{-}OPO(OH)_2$. Various debenzylating agents were tried, but in each case extensive decomposition occurred and carbon dioxide was evolved.

Experimental

Dibenzyl Carbethoxy Phosphate.—Ethyl chloroformate (8 ml., freshly distilled) was added to a suspension of silver dibenzyl phosphate[3] (m.p. 213°, 1.05 g., prepared from dibenzyl phosphorochloridate[4]) in dry dioxan (30 ml.). A precipitate formed instantly. The mixture was stirred for 2 hr. at room temperature and the precipitate of silver chloride was then filtered off. The solvents were evaporated by high vacuum distillation, yielding 0.94 g. (98%) of a colorless viscous oil, which was stored in the cold.

Anal. Calcd. for $C_{17}H_{19}O_6P$: C, 58.2; H, 5.44; P, 8.9%. Found: C, 57.8; H, 5.46; P, 9.1.

The infrared absorption of the product was measured in carbon tetrachloride solution, using a Perkin-Elmer Model 12 spectrometer. Strong absorption bands occurred at 1024 $cm.^{-1}$ (due to the POC vibration[5]), at 1235 $cm.^{-1}$ (phosphoryl stretching), at 1372 $cm.^{-1}$ (methyl group vibration), at 1459 $cm.^{-1}$ (benzyl group vibration), at 1731 $cm.^{-1}$ (carbonyl stretching), and at 2955 $cm.^{-1}$ (C–H vibration).

Hydrolysis.—Dibenzyl carbethoxy phosphate (about 100 mg.) was dissolved in aqueous dioxan (100 ml.; 1:1 by volume) in a beaker fitted with a magnetic stirrer and covered by a rubber stopper. This stopper had three holes, through which the glass and calomel electrodes as well as the capillary glass outlet of a magnetic valve-operated buret led into the solution. The beaker was placed into a thermostat at 37.0°, above a rotating permanent magnet enclosed in a brass can. The electrodes were connected to a Radiometer Model TTT 1a automatic pH meter, which was set to keep a constant pH of 6.00 ± 0.05. The buret contained standard 0.10 *N* sodium hydroxide solution and titrated the dibenzyl hydrogen phosphate as it was formed. In a separate experiment, the end point in the titration of dibenzyl hydrogen phosphate had been shown to be pH = 6.0. Example of a kinetic experiment: dibenzyl carbethoxy phosphate (initially 1.9 mmoles) at 37.0°.

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