

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.)]; $\nu_{\text{max}}^{\text{KBr}}$ 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 $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.48; H, 8.64. Found: C, 81.23; H, 8.55.

3-Methyl-3-phenyl-2-butyldenemalononitrile (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 $\text{C}_{14}\text{H}_{14}\text{N}_2$: 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-phenylisobutyldenemalononitrile (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.

Acknowledgment.—We wish to acknowledge gratefully the support of this research by a grant from the Bristol Laboratories, Division of Bristol-Myers Company, Syracuse, New York. We wish also to acknowledge the support of the National Institutes of Health to Indiana University for the purchase of the high-resolution nuclear magnetic resonance spectrometer.

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

J. REID SHELTON AND ANTONY CHAMP¹

Department of Chemistry, Case Institute of Technology,
Cleveland 6, Ohio

Received October 4, 1962

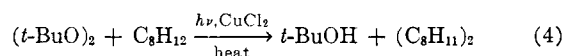
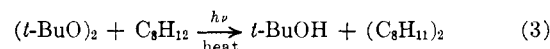
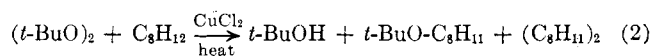
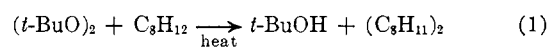
In continuation of a study of the reaction of free radicals with olefins, it became evident that further work was required to elucidate one phase of the work previously reported.²

(1) Present address: Research Laboratories, Celanese Corp., Summit, N. J.

(2) J. R. Shelton and J. N. Henderson, *J. Org. Chem.*, **26**, 2185 (1961).

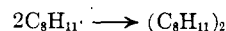
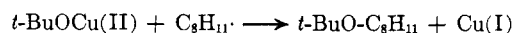
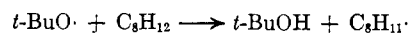
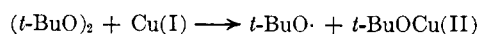
The previous work had reported that the slow photolysis of di-*t*-butyl peroxide in 4-vinylcyclohexene yielded dehydrodimers and that the more rapid copper-induced decomposition resulted in both *t*-butyl vinylcyclohexenyl ethers and dehydrodimers. Reference was made to the work of Kharasch and Fono,³ 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 Kochi⁴ 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.



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 Kochi⁴ in which a free radical R· is oxidized by a cupric salt, Cu(II)OX, to form ROX and Cu(I).



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 $\text{CH}_3\cdot$ radicals on 4-vinylcyclohexene. The spectra of two of the materials

(3) M. S. Kharasch and A. Fono, *ibid.*, **24**, 608 (1959).

(4) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

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 $\text{CH}_3\cdot$ 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 dehydromers 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 dehydromer 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 dehydromer.

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

Acknowledgment.—The authors wish to acknowledge the support of this research by the Goodyear Tire and Rubber Company.

Dibenzyl Carbethoxy Phosphate

A. LAPIDOT AND M. HALMANN

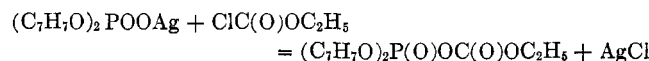
Isotope Department, The Weizmann Institute of Science,
Rehovoth, Israel

Received December 12, 1962

Several anhydrides of phosphoric acid with carboxylic acids of the type RCO—O—PO(OH)_2 have been des-

cribed,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.



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°, $k = (3.53 \pm 0.02) \times 10^{-5} \text{ sec}^{-1}$, using initial concentrations of 2 to 9 mmoles of the anhydride.

Attempts were made to remove the benzyl groups and to obtain carbethoxy phosphate, $\text{C}_2\text{H}_5\text{O C(O)—OPO(OH)}_2$. 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 phosphate³ (m.p. 213°, 1.05 g., prepared from dibenzyl phosphochloridate⁴) 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 $\text{C}_{17}\text{H}_{19}\text{O}_6\text{P}$: 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 vibration⁵), 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°.

(1) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 348.

(2) F. Lynen, *Chem. Ber.*, **73**, 367 (1940); R. Bentley, *J. Am. Chem. Soc.*, **70**, 2183 (1948); **71**, 2765 (1949); D. E. Koshland, Jr., *ibid.*, **74**, 2286 (1952). F. Lipmann, *Advan. Enzymology*, **6**, 231 (1946); A. W. D. Avison, *J. Chem. Soc.*, 732 (1955).

(3) A. R. Atherton, H. T. Openshaw, and A. R. Todd, *ibid.*, 385 (1945).

(4) G. W. Kenner, A. R. Todd, and F. J. Weymouth, *ibid.*, 3678 (1952).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuene and Co., London, 1958, p. 311.