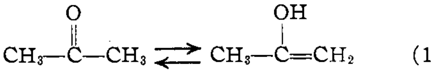
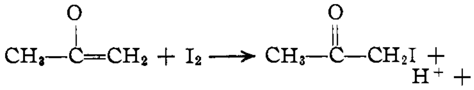
iodine and aromatic hydrocarbons,[1] and that the subsequent drop in absorption had been due to the slow reaction of iodine to form iodoacetone. We now wish to report that a more detailed investigation indicates that iodine, in the concentrations used in our absorption measurements, reacts with acetone almost instantaneously to form iodide ion and, supposedly, iodoacetone. The iodide ion evidently establishes equilibrium with the remaining iodine very quickly to form triiodide ion, which gives the strong ultraviolet band reported above. The equations are given



$$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \rightleftharpoons CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH_2} \qquad (1)$$



$$\mathrm{CH_3{-}\overset{O}{\overset{|}{C}}{=}CH_2 + I_2 \longrightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2I + H^+ + I^-} \qquad (2)$$

$$\mathrm{I^- + I_2 \rightleftharpoons I_3^-} \qquad (3)$$

The experimental evidence for our conclusions can be summed up as follows: (1) Successive additions of acetone to a solution of iodine in carbon tetrachloride caused small, progressive shifts of the normal iodine peak toward shorter wave lengths, but no absorption in the ultraviolet region. Upon standing, however, these solutions underwent a remarkable change. The absorption peak in the visible region began to drop and an absorption peak appeared in the ultraviolet having the same form and $\lambda_{\max.}$ as had been earlier observed in solutions of iodine in pure acetone. In the light of the evidence which follows we designate this as the triiodide peak. The simultaneous disappearance of free iodine and the appearance of triiodide ion is good evidence for reactions (2) and (3).

(2) When acetone containing a small amount of dissolved potassium iodide was added to a solution of iodine in carbon tetrachloride, the characteristic peak in the ultraviolet region instantly appeared and the free iodine peak was not obtained at any time. This evidence, together with the fact that triiodide ion in its aqueous solutions has an intense absorption peak[2] ($\lambda_{\max.} = 353$ mμ) almost identical in position with the peak observed above, seems to show unmistakably that triiodide ion is being formed when iodine reacts with acetone.

(3) The purified acetone used to make up our solutions was neutral toward litmus, but its iodine solutions gave a distinct acid reaction furnishing more evidence for the occurrence of reaction (2).

(4) Conductivity measurements of a 0.008 molar solution of iodine in acetone at room temperature gave a value of 90 for the molar conductivity of iodine. This value can be compared to the molar conductivity of potassium iodide, which is 100 at the same concentration and temperature.[3] The high molar conductivity of iodine in acetone furnishes definite proof that the reaction of iodine with acetone produces ionic species.

Reactions (1) and (2) are well known, from the work of Lapworth,[4] Bartlett,[5] and Ingold, *et al.*,[6] on the kinetics of the halogen–acetone reaction. These investigators have shown that reaction (1) is the rate controlling step and that the over-all reaction rate is therefore independent of the halogen concentration. We did not observe a reaction rate of this kind in our original absorption measurements because of the low concentration of iodine used (5×10^{-5} molar). It now seems evident that the minute amount of iodine reacted to completion within the time required to make up the solution.[7,8]

---

[2] W. R. Brode, This Journal, **48**, 1877 (1926).

[3] P. Walden, H. Ulrich and O. Busch, *Z. physik. Chem.*, **123**, 459 (1926).

[4] A. Lapworth, *J. Chem. Soc.*, **85**, 30 (1904).

[5] P. D. Bartlett, This Journal, **56**, 967 (1934).

[6] S. K. Hsu, C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 78 (1938).

[7] For experimental details see reference 1.

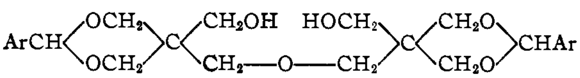
[8] We gratefully acknowledge the support of this research by the Atomic Energy Commission.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIF.
RECEIVED JANUARY 23, 1950

Acetals of Dipentaerythritol

BY ELIAHU BOGRACHOV[1]

In connection with an investigation in the pentaerythritol series,[2] it became desirable to study the hitherto unknown acetals of dipentaerythritol. When the latter is treated with aromatic aldehydes in presence of an acidic catalyst and under conditions under which the water formed is continually (azeotropically) removed, diacetals



are formed. The two remaining hydroxyl groups are incapable—at least under these conditions—of reacting with a third molecule of the aldehyde, forming an eight-membered ring; they can be acylated in the normal manner.

The diacetals decompose even in contact with humid air. This is the reason why the acetalisation of pentaerythritol according to Kraft[3] can be used for the quantitative determination of the tetrahydric alcohol in presence of dipentaerythritol.

Experimental

Preparation of Dipentaerythritol.—Friedrich and Bruen's[4] method for preparing dipentaerythritol is not satisfactory on any larger scale, and the following procedure is preferred: starting from the double compound of 4 moles of pentaerythritol and 1 mole of dipentaerythritol,[5] the former was separated as dibenzal derivative and the mother liquor evaporated to dryness. Acetylation of the residue

---

[1] Present address: Division of Plant Protection, Ministry of Agriculture, Tel-Aviv, Israel.

[2] Bograchov, This Journal, **72**, 2268 (1950).

[3] Kraft, *C. A.*, **25**, 5114 (1931).

[4] Friedrich and Bruen, *Ber.*, **63**, 2681 (1930).

[5] Wyler, U. S. Patents 2,270,839 (1942); 2,288,929 (1942); Wyler and Wernett, U. S. Patents 2,251,236 (1941), 2,299,048 (1942).

with acetic anhydride and sodium acetate gave a mixture of acetates, which was fractionated in a high vacuum (0.5 mm.). The pentaerythritol tetraacetate fraction collected between 150 and 170° and the dipentaerythritol hexaacetate at 257–262°. The latter was refluxed with dilute hydrochloric acid and the solution thus formed was concentrated. From 100 g. of the double compound, 8.5 g. of the pure dipentaerythritol, m. p. 221° (from water), was obtained.

Dibenzaldipentaerythritol.—A mixture of 2.5 g. of dipentaerythritol, 3.2 cc. of benzaldehyde, some crystals of *p*-toluenesulfonic acid and 100 ml. of benzene was heated azeotropically. When water ceased to separate, the benzene solution was treated with calcium carbonate and filtered, the benzene distilled off and the residue triturated with methanol and recrystallized from butanol; long, lancet-shaped crystals of m. p. 166° were thus obtained which decompose rapidly on exposure to humid air; yield 60%.

Anal. Calcd. for $C_{24}H_{30}O_7$: C, 67.0; H, 7.0. Found: C, 66.6; H, 7.1.

Di-(*p*-methoxybenzal)-dipentaerythritol was obtained analogously from dipentaerythritol (2.5 g.) and anisaldehyde (3.7 ml.). The crude product was triturated with dry ether and recrystallized from pyridine; m. p. 167.5°; yield 3 g. (60%).

Anal. Calcd. for $C_{26}H_{34}O_9$: C, 63.6; H, 7.0. Found: C, 63.9; H, 7.1.

Di-(*p*-nitrobenzal)-dipentaerythritol, obtained from dipentaerythritol (2.5 g.) and *p*-nitrobenzaldehyde (4.6 g.), formed an oily layer which did not dissolve in benzene. The solvent was decanted, and the product triturated with glycol monoethyl ether and washed with ether; m. p. 112° after sintering at 100°; soluble in pyridine; yield 2 g. (40%).

Anal. Calcd. for $C_{24}H_{28}O_{11}N_2$: C, 55.4; H, 5.4; N, 5.4. Found: C, 55.1; H, 5.5; N, 5.7.

Benzoylation with benzoyl chloride in pyridine gave a dibenzoate which melted at 126° (after sintering); soluble in acetone and chloroform, insoluble in ether.

Anal. Calcd. for $C_{38}H_{36}O_{13}N_2$: N, 3.9. Found: N, 4.1.

WEIZMANN INSTITUTE OF SCIENCE
DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, ISRAEL

RECEIVED OCTOBER 22, 1949

Ultraviolet Absorption Study of the Ionization of Substituted Phenols in Ethanol

BY NORMAN D. COGGESHALL AND ALVIN S. GLESSNER, JR.

In a private communication Brother Columba Curran and Professor J. L. Magee of Notre Dame University have recently pointed out improved interpretations of certain of the data previously reported under the above title.[1] The weak acidity of the hindered phenols is now to be attributed to the small difference in energy of solvation between the ions and the un-ionized molecules. This is due to the reduction of interaction energy between the ion and the solvent as a result of steric hindrance offered by the large ortho substituents. The large $\Delta(1/\lambda)$ values observed for the hindered phenols may be now regarded as a consequence of the reduction of interaction energy between the ion and solvent. This weaker interacting energy would allow the oxygen electrons to migrate more freely into the phenyl ring with a consequent increase of $\Delta(1/\lambda)$. The same considerations apply in a comparison of the $\Delta(1/\lambda)$ values for the unhindered and partially hindered phenols.

GULF RESEARCH AND DEVELOPMENT COMPANY
PITTSBURGH, PENNSYLVANIA

RECEIVED NOVEMBER 18, 1949

---

[1] N. D. Coggeshall and A. S. Glessner, Jr., THIS JOURNAL, **71**, 3150 (1949).

The Preparation and Polymerization of Diallyl Cyclohexanephosphonate

BY A. J. CASTRO[1] AND W. E. ELWELL

The interest in allyl resins and the use of esters of phosphoric acid as plasticizers because of the flame resistance thereby imparted[2] prompted an investigation of the possibility of preparing a fire resistant resin from diallyl cyclohexanephosphonate. The synthesis of this ester and its polymerization are described in this report.

Experimental

Diallyl Cyclohexanephosphonate.—Thirty-seven and eight-tenths grams of cyclohexanephosphonyl chloride[3] and 59.5 g. of pyridine were mixed in a flask equipped with a short condenser having a calcium chloride tube attached at the top. During mixing, the solution warmed and became yellow in color. The calcium chloride tube was removed periodically and 43.7 g. of allyl alcohol was added portionwise through the condenser during a period of ten minutes. The first addition of alcohol was accompanied by the evolution of considerable heat and the reaction flask was immersed in an ice-bath while the remainder was added. A white solid precipitated from solution during this period. The reaction mixture was allowed to stand overnight while the ice melted and the system came to room temperature. The mixture was stirred with 400 ml. of water and the oil that separated was removed. The cloudy aqueous layer was extracted with ether and the combined ether–oil mixture was washed with water and dried over anhydrous sodium sulfate. The addition of a small amount of salt was found to be a convenient aid in destroying the emulsion that formed during the water washing. The ether was evaporated from the dried and filtered solution and the remaining oil distilled. Twenty-five and six-tenths grams (55.7%) of diallyl cyclohexanephosphonate was collected at 117–134° (1.8–3.0 mm.). This product was redistilled for analysis and substantially the entire volume boiled at 119.5–119.7° (1.95–2.2 mm.). Unsaturation in this product was demonstrated by the decoloration of a carbon tetrachloride solution of bromine.[4]

The ester is a colorless liquid possessing a faint garlic-like odor; $n^{20}\text{D}$ 1.4760; d^{20}_4 1.0548.

Anal. Calcd. for $C_{12}H_{21}PO_3$: P, 12.68. Found: P, 12.40, 12.45.

On the basis of the observed refractive index and density and the calculated molecular weight, the molecular refraction (*M*D) for this compound is found to be 65.32. Using the values for the group refractivities[5] for carbon, hydrogen and the double bond, reported[6] refractive in-

---

[1] Present address: Chemistry Department, University of Santa Clara, Santa Clara, California.

[2] Simonds and Ellis, "Handbook of Plastics," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 101.

[3] Kindly furnished by J. O. Clayton and W. L. Jensen, THIS JOURNAL, **70**, 3880 (1948).

[4] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 36.

[5] Lange, "Handbook of Chemistry," 3rd ed., Handbook Publishers, Inc., Sandusky, Ohio, 1939, p. 855.

[6] Kosolapoff, THIS JOURNAL, **67**, 1180 (1945).