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.

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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.

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[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-

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[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).