+3.08°, in 100 ml. of 10% hydrochloric acid was refluxed for a period of 4 hr. The clear solution was cooled, saturated with sodium chloride and extracted continuously with diethyl ether for 18 hr. The ethereal extract was dried over anhydrous magnesium sulfate and the ether removed by distillation through an 8-in. packed column. Distillation of the residual liquid yielded 16.2 g. of a mixture of *d*-2-butanol and ethanol, b.p. 78–83°, $n^{25}\text{D}$ 1.3713. Using the value $n^{25}\text{D}$ 1.3590 for ethanol, the concentration of the 2-butanol in the distillate was calculated as 46.8% by weight, and the specific rotation of the optically active 2-butanol as $[\alpha]^{25}\text{D}$ +8.70° (75.2% retention).

Transesterification of *l*-2-Butanol and Triethyl Phosphite.—This transesterification was carried out in exactly the same manner as described for the optical isomer. *l*-2-Butanol (35 g.) and 166 g. of triethyl phosphite, gave during a 12-hr. heating period with a final reaction temperature of 165°, a yield of 38.7 g. of (*l*)-2-butyl diethyl phosphite, b.p. 68–69° (12 mm.), $n^{25}\text{D}$ 1.4176, $[\alpha]^{25}\text{D}$ −2.94° (neat).

Anal. Calcd. for $C_8H_{19}O_3P$: C, 49.47; H, 9.86; P, 15.95. Found: C, 49.15; H, 9.85; P, 15.99.

Hydrolysis of (*l*)-2-Butyl Diethyl Phosphite.—The hydrolysis of 34.5 g. of (*l*)-2-butyl diethyl phosphite in 100 ml. of 10% hydrochloric acid was performed exactly as described for the (*d*)-isomer. Distillation of the crude hydrolysis product gave 10.0 g. of material, b.p. 85–99°, $n^{25}\text{D}$ 1.3848, containing 80.3% of *l*-2-butanol with a specific rotation of $[\alpha]^{25}\text{D}$ −5.68° (74.7% retention).

Hydrolysis of Diethyl Neopentyl Phosphite.—A two-phase system composed of 25 g. of diethyl neopentyl phosphite and 100 ml. of 10% hydrochloric acid was refluxed for 4 hr. The cooled reaction mixture was then made basic with potassium carbonate and extracted with several small portions of ether. After drying with anhydrous magnesium sulfate and Drierite, the ethereal extract was distilled under a small column to remove the solvent. Distillation of the liquid residue yielded 7.4 g. (70%) of material, b.p. 111–114°. The α-naphthylurethan derivative, m.p. 97–98°, of the distillate showed no depression of the melting point when mixed with the α-naphthylurethan derivative of authentic neopentyl alcohol.

Transesterification of 2,2,2-Trichloroethanol and Triethyl Phosphite.—The experimental conditions, the yield of mixed phosphite and the analysis are listed in Tables I and II.

In addition to the main product of the reaction, diethyl 2,2,2-trichloroethyl phosphite, there was obtained upon fractionation of the reaction mixture a cut of 20.8 g. of colorless oily distillate, b.p. 50° (0.65 mm.), $n^{25}\text{D}$ 1.4367. This product, which amounted to a yield of approximately 8% of the trichloroethanol employed in the run, gave analytical values in close agreement with those calculated for diethyl 2-hydroxy-1,1-dichloroethylphosphonate, $(C_2H_5O)_2P(O)CCl_2\text{-}CH_2OH$, the postulated product of a Michaelis–Arbuzov condensation between trichloroethanol and triethyl phosphite.

Anal. Calcd. for $C_6H_{13}Cl_2PO_4$: C, 28.7; H, 5.2; Cl, 28.25; P, 12.34. Found: C, 31.6; H, 5.7; Cl, 28.45; P, 11.94.

The product was found to contain 2.96% of tervalent phosphorus, possibly indicating contamination by the mixed phosphite, the main product of the reaction.

Acknowledgment.—We are indebted to the personnel of Analytical Branch, Chemical Research Division, Chemical Warfare Laboratories, for performing all analyses reported in this paper.

ARMY CHEMICAL CENTER, MARYLAND

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

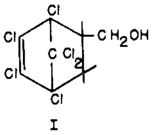
Thiophosphoryl Derivatives of the Adducts from Hexachlorocyclopentadiene and Unsaturated Alcohols

BY ELLIS K. FIELDS

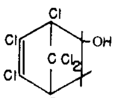
RECEIVED AUGUST 2, 1956

Three new adducts of hexachlorocyclopentadiene with unsaturated alcohols have been prepared and converted, along with the allyl alcohol adduct, to twelve derivatives in high yield. The dithiophosphoric acids and the related succinic acids are effective extreme-pressure additives for lubricating oils.

Stable alcohols containing a high percentage of chlorine are not readily available. A general method of preparing such alcohols is the reaction of hexachlorocyclopentadiene with unsaturated alcohols. Earlier work showed that hexachlorocyclopentadiene reacts with allyl alcohol to give the adduct I in good yield.[1] Three new adducts of hexachlorocyclopentadiene with vinyl alcohol (II), 3-cyclohexene-1-methanol (III) and 3-cyclohexene-1,1-dimethanol (IV) have now also been prepared.



I



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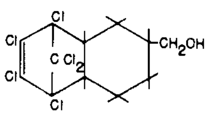

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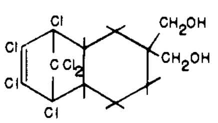
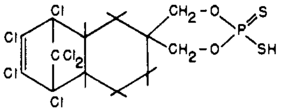
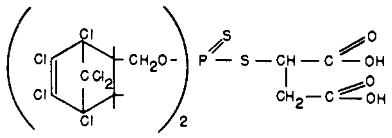


IV

Twelve derivatives of hexachlorocyclopentadiene adducts have been made in high yield. All four adducts were converted to the dithiophosphoric acids by reaction with phosphorus pentasulfide; molecular weight determinations show that the dithiophosphoric acid of IV has the cyclic structure V. From I dithiophosphoric acid, the zinc and lead salts were made. The dithiophosphoric acids from I and II were added to maleic anhydride to give substituted mercaptosuccinic acids; that derived from I is VI. The borate and *p*-toluenesulfonate of I were prepared, and thiophosphates were made from I and II with thiophosphoryl chloride. Properties of the twelve derivatives are listed in Table I.



V



VI

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[1] E. K. Fields, THIS JOURNAL, **76**, 2709 (1954).

TABLE I

DERIVATIVES OF ADDUCTS OF HEXACHLOROCYCLOPENTADIENE AND UNSATURATED ALCOHOLS

Derivative	Yield, %	M.p., °C. or n^{20}_{D}	Chlorine, %		Sulfur, %		Phosphorus, %		Mol. wt.
			Calcd.	Found	Calcd.	Found	Calcd.	Found	
Allyl alcohol adduct I									
Dithiophosphoric acid	98	1.5965	56.38	56.10	8.48	8.60	4.10	4.10	760
Zn salt	94	1.5882	54.04	53.80	8.13	7.85	3.94	3.70	[a]
Pb salt	98	194–196	49.50	49.60	7.45	7.90	3.61	3.70	[b]
Succinic acid	78	1.5539	48.85	48.60	7.35	7.12	3.56	3.31	860
Borate	96	232–233	64.02	64.00	...	...	..	..	[c]
p-Toluenesulfonate	93	130–131	43.87	43.60	6.60	6.45	..	..	476
Thiophosphate	97	1.5240	60.30	60.40	3.05	3.20	2.95	2.80	1090
Vinyl alcohol adduct II									
Adduct	92	155	67.16	67.00	...	...	..	..	307
Acetate	89	44[d]	59.30	59.10	...	...	..	..	349
Dithiophosphoric acid	96	1.6965	58.60	58.80	8.83	8.75	4.27	4.15	700
Succinic acid	93	143	50.52	50.26	7.60	7.83	3.68	3.42	835
Thiophosphate	84	1.5378	63.16	62.90	3.17	3.08	3.07	2.96	..
3-Cyclohexene–1-methanol adduct III									
Adduct	67	[e]	55.30	55.10	...	...	..	..	381
Dithiophosphoric acid	96	1.5761	49.30	49.00	7.42	7.63	3.59	3.68	850
3-Cyclohexene–1,1-dimethanol adduct IV									
Adduct	91	133	51.13	50.90	...	...	..	..	416
Dithiophosphoric acid	84	206–207	41.60	41.40	12.57	12.58	6.09	5.90	510

[a] Zn, calcd. 4.16, found 3.97. [b] Pb, calcd. 12.05, found 10.90. [c] B, calcd. 1.09, found by emission spectroscopy 2.00. [d] B.p. 113° at 0.6 mm. [e] B.p. 192–194° at 0.65 mm.

These hexachlorocyclopentadiene derivatives are a new class of compounds containing large amounts of chlorine with sulfur and phosphorus. The dithiophosphoric acids are effective extreme-pressure additives for lubricating oils. The succinic acids are even more effective than the parent compounds, possibly because of stronger chemisorption of the two carboxyl groups by the metal surface.

Experimental

Vinyl acetate, 3-cyclohexene–1-methanol and 3-cyclohexene–1,1-dimethanol were obtained from Carbide and Carbon Chemicals Corp.; hexachlorocyclopentadiene, from Hooker Electrochemical Corporation; distilled phosphorus pentasulfide and thiophosphoryl chloride, from Victor Chemical Corporation; other reagents and intermediates, from Eastman Kodak Co. All were used as received.

Adducts I, III and IV were prepared by heating equimolar quantities of the unsaturated alcohols and hexachlorocyclopentadiene at 130° for 24 hr., then distilling or crystallizing. Adduct II was made by hydrolysis of the adduct of vinyl acetate with hexachlorocyclopentadiene. The vinyl acetate adduct was prepared by refluxing equimolar quantities of vinyl acetate with hexachlorocyclopentadiene until the pot temperature reached 150°. Distillation gave 89% of viscous, colorless adduct. A solution of 36 g. (0.1 mole) of vinyl acetate adduct in 75 ml. of ethanol was stirred and refluxed with 50 ml. of concentrated hydrochloric acid for 2 hr. The clear solution was poured into 600 ml. of water and stirred with occasional scratching until the alcohol adduct solidified. Recrystallization from *n*-heptane gave 28.2 g. of white crystals.

To make the dithiophosphoric acids, a mixture of 0.2 mole of alcohol adduct and 0.05 mole of phosphorus pentasulfide in 150 ml. of xylene was stirred at 120° until all the solid had disappeared (30 minutes to 2 hours) and for 2 hr. more. The solution was then evaporated under vacuum.

The zinc salt of the dithiophosphoric acid of I was made from zinc oxide, the lead salt from basic lead carbonate. In both cases, excess reagent was employed and the unreacted portion was filtered off.

To make the dithiophosphorylsuccinic acids, equimolar quantities of the dithiophosphoric acid and maleic anhydride in isopropyl ether were refluxed for 14 hr., one equivalent of water was added, and refluxing was continued for 2 hr. more. The ether solution was evaporated on a steam-bath, and the residue was taken up in 1:1 benzene–*n*-heptane, filtered and again evaporated. The solid acid was recrystallized from 1:4 benzene–*n*-heptane.

The borate of I was prepared by blowing dry air through a mixture of 0.15 mole of tri-*n*-butyl borate and 0.45 mole of I. Over a period of 4 hr. the temperature was raised from 104 to 145° at 100 mm. as 39 ml. of liberated butanol distilled. The solid product left in the reaction flask was recrystallized from *n*-heptane. The *p*-toluenesulfonate of I was prepared from equimolar quantities of *p*-toluenesulfone chloride and I in pyridine at 65° for 1 hr.

To make the thiophosphates, 0.2 mole of thiophosphoryl chloride was added dropwise to a stirred solution of 0.6 mole of the alcohol adduct and 0.6 mole of pyridine in 400 ml. of toluene at 75°. The mixture was then stirred 18 hr. at 110°, cooled, filtered from the pyridine hydrochloride and evaporated under vacuum. The residue was dissolved in 700 ml. 1:1 benzene–*n*-heptane, filtered and again evaporated under vacuum.

WHITING, INDIANA