mann[4] with *n*-propylamine, and the present study with isobutylamine, the rounded-off figures given below are obtained for the alcohols:

Amine	Rearrangement, %	Migration of H relative to CH_3
Ethyl	2	..
n-Propyl	80	25[a]
Isobutyl	90	5[b]
Neopentyl	~100[c]	..

[a] Corrected by a statistical factor of 2 favoring H relative to CH_3 migration. [b] Corrected by a statistical factor of 2 favoring CH_3 relative to H migration. [c] Inferred from the results of M. Freund and F. Lenze, *Ber.*, **24**, 2150 (1891).

It is apparent that substitution of methyl for hydrogen on the β-carbon atom greatly facilitates rearrangement,[20] the effect being larger for methyl than hydrogen migration.

Since the products of the isobutylamine–nitrous acid reaction are rate controlled, the product ratios obtained (Table I) provide measures of the relative rates of migration. On this basis the data permit the estimate that the energy of activation for hydrogen migration is about 2.5 cal. lower than for methyl migration, but the entropy of activation favors the latter (based on the migration of one methyl) by about 5 cal./deg.

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(20) Similar results have been obtained and discussed for anchimeric assistance in solvolysis reactions, *cf.* S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND, AND FROM THE CHEMICAL CORPS, CHEMICAL WARFARE LABORATORIES, ARMY CHEMICAL CENTER, MARYLAND]

The Transesterification of Trialkyl Phosphites with Aliphatic Alcohols[1,2]

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Trialkyl phosphites undergo an uncatalyzed alcohol exchange reaction when heated with aliphatic alcohols to yield mixtures of tertiary phosphites containing different alkyl groups. The scope of this reaction was investigated and a probable mechanism for the reaction postulated. The yields of the mono- and ditransesterified trialkyl phosphites were found to be dependent on the ratio of alcohol to phosphite employed. The results of this study indicate that the exchange reaction of a trialkyl phosphite with an alcohol having a larger alkyl group than the ester is a general reaction which can be applied to the preparation of mixed trialkyl phosphites.

While the transesterification with alcohols is a well-established procedure in the carboxylic ester series, little information is available on this type of reaction involving esters of phosphorous acid. Diethyl hydrogen phosphite (phosphonate) has been reported[4] to undergo an exchange reaction with aliphatic alcohols with the formation of mixed dialkyl hydrogen phosphites, but the literature does not contain any information on a similar exchange reaction of trialkyl phosphites. However, triaryl phosphites are known to undergo transesterification with aliphatic alcohols[5,6] yielding mixed alkyl aryl esters. In general, mixed trialkyl esters of phosphorous acid have been prepared in the past from phosphorochloridites or -dichloridites and alcohols or sodium alkoxides in yields varying between 13 and 50%.[5,7]

The present investigation was undertaken to determine the usefulness of the transesterification reaction between alcohols and trialkyl phosphites as a practical method for the preparation of mixed trialkyl phosphites and to elucidate a mechanism for this reaction. The technique used in this study for transesterifying trialkyl phosphites with alcohols was similar to that applied by Kosolapoff[4a] in the transesterification of diethyl hydrogen phosphite. The trialkyl phosphites were refluxed at atmospheric pressure with alcohols having larger alkyl groups than the starting ester, and the lower alcohol was distilled from the reaction mixture at the rate of its formation.

The results of our investigation indicate that the transesterification of trialkyl phosphites is a general reaction which can be applied advantageously to the preparation of mixed trialkyl phosphites. Since the exchange reaction proceeds in three steps with apparently equal or almost equal rates, only a

$$R'OH + (RO)_3P \rightleftarrows R'OP(OR)_2 + ROH$$
$$R'OH + R'OP(OR)_2 \rightleftarrows (R'O)_2POR + ROH$$
$$R'OH + (R'O)_2POR \rightleftarrows (R'O)_3P + ROH$$

moderate yield of the monotransesterification product is obtained, if the phosphite and alcohol are used in equimolar amounts. However by a proper choice of the ratio of the reactants any one of the three transesterification products can be made the main reaction product.

A limitation of the transesterification reaction as a preparative method is the fact that the alcohol to be exchanged must have a boiling point which is not too close to that of the exchanging alcohol; otherwise, the reaction cannot be forced by distilling off the originally esterified alcohol, and difficulty is encountered in the separation of the products from the original phosphite. An example of

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(1) The material presented in this paper represents a portion of a thesis submitted by Richard J. Ess to the University of Maryland in partial fulfillment of the requirements of the M.S. degree, July, 1955.

(2) Presented in part at the 129th Meeting of the American Chemical Society in Dallas, Texas, April 8–13, 1956.

(3) To whom inquiries concerning this paper should be directed; address: Research Directorate, Army Chemical Center, Md.

(4) (a) G. M. Kosolapoff, THIS JOURNAL, **73**, 4989 (1951). (b) B. A. Arbuzov and V. S. Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, **83**, 79 (1952); *C. A.*, **47**, 2685*a* (1953). (c) V. K. Kuskov and T. Kh. Gradia, *ibid.*, **92**, 323 (1953); *C. A.*, **49**, 155g (1955).

(5) S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

(6) F. C. Gzemski, U. S. Patent 2,253,558 (1944); *C. A.*, **38**, 6548[6] (1944).

(7) The literature on this subject has been reviewed by Kosolapoff in "Organic Phosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 184–187.

this limitation is the transesterification of 2,2,2-trifluoroethanol, b.p. 74°, with triethyl phosphite, which yielded only about 4% of the desired monotransesterified product.

The results of several transesterifications carried out between *n*-butyl alcohol and triethyl phosphite in the presence of small amounts of aluminum chloride or sodium (Table I, runs 5, 6, 9 and 10) showed that the reaction is catalyzed by these reagents. The ethanol formed in the reaction began to distil at a pot temperature which apparently was 20° lower than in the absence of the catalysts. In the only run (no. 7) carried out in the presence of small amounts of added diethyl phosphonate, the same catalytic effect was observed as with aluminum chloride or sodium. Tetraethyl titanate which catalyzes the transesterification of carboxylic acid esters was found to be ineffective in the transesterification of trialkyl phosphites. Since the alcohol exchange reactions with the phosphites were driven to completion by heating the reaction mixture until the lower boiling alcohol ceased to distil, the yields of the various products were not noticeably influenced by the presence of the catalysts.

The effect of sodium (run 3) or aluminum chloride (run 2) was very pronounced in the reaction of 2-butanol with triethyl phosphite. With catalytic amounts of these promoters, the transesterification takes place very readily to yield on the basis of the phosphite consumed approximately 60% of diethyl 2-butyl phosphite with a conversion of about 70%; at the same time about 17% of ethyl bis-(2-butyl)-phosphite is obtained. In the absence of a promoter (run 1), the reaction proceeded with only 12% conversion at such a slow rate that the ethanol cannot be removed continuously from the reaction mixture without the co-distillation of 2-butanol. In a similar, uncatalyzed run (no. 4) employing 1-butanol instead of 2-butanol, a yield of about 55% of butyl diethyl phosphite was obtained with over 60% conversion; the yield of dibutyl ethyl phosphite amounted to approximately 23%.

The yields of the monotransesterification products can be increased by increasing the molar ratio of trialkyl phosphite to alcohol (runs 8, 9 and 10), while higher yields of the di- and tritransesterification products are readily obtained with larger amounts of the alcohol, *i.e.*, a phosphite to alcohol ratio smaller than one (runs 11, 12 and 13).

In the transesterification reaction between triethyl phosphite and neopentyl alcohol (run 16), the yield of diethyl neopentyl phosphite was slightly lower and the yield of ethyl dineopentyl phosphite slightly higher than the yields of the corresponding phosphites in run 8. Similar results were also obtained in run 14 with benzyl alcohol.

Negatively substituted alcohols, such as 2,2,2-trichloro- and 2,2,2-trifluoroethanol, underwent the transesterification in the same manner as the unsubstituted alcohols. However, in a run (no. 15) with trichloroethanol, a side reaction occurred when the internal temperature of the reaction mixture reached approximately 170° to yield approximately 8% of a material which boiled at a pressure of 3 mm. about 6° lower than the main reaction product, diethyl 2,2,2-trichloroethyl phosphite. The analysis of the by-product agreed with the calculated values for the postulated Michaelis–Arbuzov condensation product, $(C_2H_5O)_2P(O)CCl_2$-CH_2OH.

The attempted transesterification of two moles of triethyl phosphite with one mole of 1-butanol at reflux temperature (105°) during a 12-hr. period yielded only unchanged starting materials. Since this failure might have been the result of an insufficient reaction temperature for the transesterification of a tertiary alcohol, equimolar quantities of triethyl phosphite and the next higher tertiary alcohol, *t*-amyl alcohol, were heated under the usual conditions. The mixture began to boil at 113°, and the reflux temperature gradually increased to 170° during the 16-hr. heating period. The resulting products were ethanol, diethyl phosphonate and a mixture of 2-methyl-2-butene and 2-methyl-1-butene. It is not known whether the alcohol was dehydrated, and the liberated water hydrolyzed the triethyl phosphite, or whether a transesterification took place, and the mixed phosphite immediately decomposed thermally to an alkene and diethyl phosphonate.

Triisopropyl phosphite was found to undergo transesterification in the same manner as triethyl phosphite when heated with benzyl alcohol or 1-butanol. The yields of the monotransesterified products were slightly better than in the reaction of butanol with triethyl phosphite in the same ratio (1:1).

In analogy to the mechanism of the acid-catalyzed hydrolysis of phosphites,[8] the uncatalyzed or acid-catalyzed transesterification of such esters may follow a mechanism similar to that well-known in the carboxylate ester series. Since the possibility of an expansion of the normal electron octet, or in other words *d*-orbital resonance, has been accepted generally for elements of the second and higher rows of the periodic system,[9] the transesterification of phosphites can also be formulated as involving a transition state with a decet of electrons around the phosphorus atom. This formulation is preferred to that involving the attack of the proton on the phosphorus atom with the formation of a phosphonium type ion, $[(RO)_3P{:}H]^+$, because of the formal resemblance of the latter to the generally accepted intermediate of the Michaelis–Arbuzov reaction in which the phosphorus atom undergoes undoubtedly a change of covalency.

Another acceptable speculation with regard to the mechanism of the transesterification might be a reaction sequence involving the electrophilic attack of an alkyl carbonium ion on one of the oxygen atoms of the ester with a simultaneous release of one of the original alkyl groups as carbonium ion. However, that the transesterification of phosphites does not, or at least not exclusively, proceed through intermediate *free*, classical carbonium ions was demonstrated by employing optically active 2-butanol as well as neopentyl alcohol. If free carbonium ions were involved in the exchange reaction as formulated by the above equation, the mixed phos-

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[8] H. K. Garner and H. J. Lucas, This Journal, **72**, 5497 (1950).

[9] (a) W. von E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955); (b) D. P. Craig, *et al.*, *J. Chem. Soc.*, 332 (1954); (c) M. L. Kilpatrick and M. Kilpatrick, *J. Phys. Colloid Chem.*, **53**, 1385 (1949).

phite resulting from the optically active alcohol would be inactive, and the phosphite from the neopentyl alcohol would be the derivative of *t*-amyl alcohol. However, retention of the optical activity to an extent of about 75% was observed in the transesterification of triethyl phosphite with *d*- and *l*-2-butanol and subsequent hydrolysis with 10% hydrochloric acid, and no rearrangement of the neopentyl carbon skeleton[10] was noticed in the transesterification–hydrolysis cycle with neopentyl alcohol.

These observations indicate that the main reaction involves a cleavage of the phosphorus–oxygen and not of the carbon-to-oxygen bond during both the transesterification with the active alcohol and the hydrolysis of the mixed phosphite and exclude a mechanism involving free carbonium ions; they exclude, furthermore, an inversion of the optical activity in each of the two steps of the cycle.

On the basis of the available experimental results no preferential choice can be made between the two mechanisms postulated for the acid-catalyzed transesterification. A similar situation prevails with regard to the mechanisms which can be postulated for the base-catalyzed reaction. This exchange reaction can be formulated similarly involving either a displacement mechanism or a nucleophilic attack by the alkoxide ion on the phosphorus atom with a simultaneous expansion of the normal eight-electron shell to a decet.

Experimental[11]

Starting Materials.—The triethyl and triisopropyl phosphite were procured from Virginia–Carolina Chemical Corporation and were of a technical grade. The phosphites were purified by vacuum distillation through a 4-ft. column packed with glass helices, treatment of the distillate with small pieces of sodium to remove any dialkyl hydrogen phosphite and subsequent redistillation of the distillate. Triethyl phosphite, b.p. 52° (12 mm.), n^{25}D 1.4108; triisopropyl phosphite, b.p. 58–59° (7 mm.), n^{25}D 1.4082.

2,2,2-Trichloroethanol, b.p. 61° (18 mm.), n^{25}D 1.4881, was prepared in 56% yield by the reduction of chloral with sodium borohydride[12]; the once-distilled product assumed a bluish purple color on standing for a few days but remained colorless upon redistillation.

The addition of one mole of methyl formate to two moles of *t*-butylmagnesium chloride in diethyl ether solution yielded neopentyl alcohol, m.p. 42–44° (uncor.), b.p. 111–114°, in 41% yield.[13] The other alcohols used in this investigation were obtained from commercial sources and used without further purification.

Transesterification. General Procedure.—All transesterification runs were carried out in a round-bottomed flask of suitable size fitted with a side-arm thermometer and an 8-in. electrically heated fractionating column packed with Penn State 0.16 × 0.16-in. pertruded nickel packing. The fractionating column was surmounted by a variable take-off still-head fitted with a vapor thermometer and a receiving flask. The reaction mixture, consisting of the appropriate phosphite and alcohol, was placed into the reaction flask together with several porous-plate boiling chips and slowly heated with an electric heating mantle to reflux. The liberated, lower boiling alcohol was removed through the still-head and collected in the attached receiver until the head temperature began to drop, indicating the completion of the exchange reaction. The temperature of the reaction mixture gradually increased during this procedure. The distilled alcohol usually amounted to 70 to 95% of the theoretical yield. Except where stated otherwise, the reaction mixture was then fractionated under reduced pressure through an electrically heated 4-ft. column packed with Penn State pertruded nickel.

The results of a number of transesterifications of triethyl phosphite with various alcohols are listed in Table I. With the exception of one run these experiments were carried out using one- or two-mole quantities of the triethyl phosphite. The physical constants and analytical values for the resulting mixed trialkyl phosphites are given in Table II.

Exchange runs involving another trialkyl phosphite or a modification of the general technique are described in detail.

Transesterification of 1-Butanol and Triisopropyl Phosphite.—A solution of 1 mole (208.3 g.) of triisopropyl phosphite and 1 mole (74.1 g.) of 1-butanol was heated for 4 hr. under an 8-in. packed column. Isopropyl alcohol began to distil from the reaction mixture when a pot temperature of 125° was reached and continued to a reaction temperature of 165°. Distillation of the residual reaction mixture through a 4-ft. column yielded 0.261 mole of unchanged triisopropyl phosphite and 0.428 mole (57.9%) of diisopropyl butyl phosphite, b.p. 49–51° (3 mm.), n^{25}D 1.4177.

Anal. Calcd. for $C_{10}H_{23}O_3P$: C, 54.0; H, 10.4; P, 13.94. Found: C, 53.9; H, 10.3; P, 14.16.

A mixture, weighing 44 g., of diisopropyl butyl phosphite and isopropyl dibutyl phosphite, b.p. 51° (3 mm.) to 60° (1 mm.), was also obtained.

Transesterification of Benzyl Alcohol and Triisopropyl Phosphite.—A mixture of 1 mole (208.3 g.) of triisopropyl and 1 mole (108.1 g.) of benzyl alcohol was heated under the same conditions as described for the transesterification of triisopropyl phosphite with butanol. Distillation of isopropyl alcohol from the mixture began at a pot temperature of 123° and continued for a period of 6 hr. until a pot temperature of 193° was reached. Fractionation of the residual mixture through an 8-in. packed column yielded 0.229 mole of unreacted triisopropyl phosphite and 0.490 mole (63.5%) of diisopropyl benzyl phosphite, b.p. 73–75° (0.22 mm.), n^{25}D 1.4808.

Anal. Calcd. for $C_{13}H_{21}O_3P$: C, 60.9; H, 8.3; P, 12.09. Found: C, 61.0; H, 8.3; P, 12.18.

A mixture (63.0 g.) of diisopropyl benzyl phosphite and isopropyl dibenzyl phosphite with a boiling range from 75° (0.22 mm.) to 148° (0.45 mm.) was also obtained.

Attempted Transesterification of *t*-Butyl Alcohol and Triethyl Phosphite.—Two moles (332.4 g.) of triethyl phosphite and 1 mole of *t*-butyl alcohol (74.1 g.) were mixed and subjected to the conditions of the general transesterification procedure. The reaction mixture began to reflux at 103° and the pot temperature remained constant during a reflux period of 12 hr. Fractionation of the reaction mixture through a column yielded only two fractions: *t*-butyl alcohol, b.p. 81–84°, n^{25}D 1.3853 (lit.[14] 82.5°, n^{20}D 1.3878), and triethyl phosphite, b.p. 50–52° (12 mm.), n^{25}D 1.4106 (lit.[15] b.p. 51–52°, n^{25}D 1.4105).

Attempted Transesterification of *t*-Amyl Alcohol and Triethyl Phosphite.—One mole (166.2 g.) of triethyl phosphite and 1 mole (88.1 g.) of *t*-amyl alcohol were mixed and heated in the usual fashion. The reaction mixture started to boil when a pot temperature of 115° was reached; the temperature of the distillate varied between 32 and 79° depending on the reflux ratio. The mixture reached a final temperature of 170° during a heating period of 16 hr.

Fractionation of the distillate yielded 43.1 g. (0.61 mole) of a mixture of 2-methyl-2-butene and 2-methyl-1-butene,[16] b.p. 32.5–33.2°, n^{25}D 1.3617. A higher boiling fraction of 33.8 g. of colorless distillate, b.p. 75–79°, n^{25}D 1.3617, was identified as ethanol.

Fractionation of the reaction mixture under diminished pressure yielded 109.4 g. (0.79 mole) of diethyl hydrogen phosphite, b.p. 70–74° (10 mm.), n^{25}D 1.4058 (lit.[17] b.p. 75° (15 mm.), n^{25}D 1.4062).

Transesterification of 2,2,2-Trifluoroethanol and Triethyl Phosphite.—A mixture of 1 mole (166 g.) of triethyl phos-

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(10) F. C. Whitmore and G. H. Fleming, *J. Chem. Soc.*, 1269 (1934).

(11) All boiling points are uncorrected.

(12) S. W. Chaikin and W. G. Brown, This Journal, **71**, 122 (1949).

(13) L. H. Sommer, H. D. Blankman and P. C. Miller, *ibid.*, **76**, 803 (1954)

(14) J. W. Brühl, *Ann.*, **203**, 17 (1880).

(15) R. S. Schreiber, "Organic Syntheses," Vol. XXXI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 111.

(16) The identity of the components of the olefin mixture was established by infrared analysis which was performed by Mr. Harold Feingold.

(17) B. A. Arbuzov and V. S. Vinogradova, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 617 (1947); *C. A.*, **42**, 5844*h* (1948).

TABLE I

TRANSESTERIFICATION OF TRIETHYL PHOSPHITE WITH SEVERAL ALCOHOLS

Run	Alcohol used	Molar ratio $(EtO)_3P$/ROH	Catalyst (0.5 g.)	Reaction temp., °C.	Reaction time, hr.	$(EtO)_3P$ reacted	Yield,[a] %		
							$(EtO)_2POR$	$(RO)_2POEt$	$(RO)_3P$
1	*sec*-C_4H_9OH	1:1	None	105–155[b]	15	12.0	53.5	..	..
2	*sec*-C_4H_9OH	1:1	$AlCl_3$	96–140	4	71.8	60.7[c]	15.6[c]	..
3	*sec*-C_4H_9OH	1:1	Na	93–141	4	70.0	60.8	18.2	..
4	*n*-C_4H_9OH	1:1	None	120–170	8	63.4	56.1	15.8	6.9[d]
5	*n*-C_4H_9OH	1:1	$AlCl_3$	93–170	4	68.1	58.0	22.8	..
6	*n*-C_4H_9OH	1:1	Na	95–180	10	74.2	51.8	24.0	7.6[d]
7	*n*-C_4H_9OH	1:1	$(C_2H_5O)_2POH$[e]	93–170	4	68.2	57.2	22.8	..
8	*n*-C_4H_9OH	2:1	None	113–158	7	41.5	78.1	13.1	..
9	*n*-C_4H_9OH	2:1	$AlCl_3$	95–162	6	44.6	65.8	10.5	..
10	*n*-C_4H_9OH	2:1	Na	95–160	7	46.4	72.3	4.2[c]	4.6[d]
11	*n*-C_4H_9OH	1:2	None	93–165	4	92.7	28.1	36.0	27.9[c]
12	*n*-C_4H_9OH	1:2	$AlCl_3$	93–162	6	91.9	31.7	43.2	13.8
13	*n*-C_4H_9OH	1:2	Na	93–165	4	95.2	24.4	40.1	17.4
14	$C_6H_5CH_2OH$	2:1	None	95–150	4	40.9	67.0	23.7[d]	..
15	CCl_3CH_2OH[f]	2:1	None	120–170	6	49.5	52.8	2.4[d]	..
16	$(CH_3)_3CCH_2OH$[g]	2:1	None	120–161	4	43.1	60.2	18.7[d]	..

[a] Based on triethyl phosphite consumed. [b] The mixture of the reactants was refluxed for 8 hr. and then distilled to remove the ethanol over a period of 7 hr. [c] Yield of crude, distilled product. [d] Liquid residue from the reaction mixture. [e] 0.5 mole per cent. [f] Additional information concerning this run is given in the experimental part. [g] The experiment was performed with 0.54 mole of neopentyl alcohol and 1.08 moles of triethyl phosphite.

TABLE II

PHYSICAL CONSTANTS AND ANALYTICAL DATA OF VARIOUS MIXED PHOSPHITES

Compound	B.p.		$n^{25}D$	Carbon, %		Hydrogen, %		Phosphorus, %	
	°C.	Mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found
sec-$C_4H_9O(OC_2H_5)_2$	68–69	12	1.4174	49.47	49.3	9.86	9.7	15.95	15.84
(*sec*-$C_4H_9O)_2POC_2H_5$	86–87	11	1.4219	54.04	53.8	10.45	10.6	13.94	13.94
$(C_2H_5O)_2POC_4H_9$-*n*	75–76	12	1.4202	49.47	49.6	9.86	9.9	15.95	15.98
(*n*-$C_4H_9O)_2POC_2H_5$	102–103	10	1.4260	54.04	53.7	10.45	10.3	13.94	14.05
$(C_2H_5O)_2POCH_2C_6H_5$	85–88	1	1.4905	57.88	57.6	7.51	7.6	13.57	13.73
$(C_2H_5O)_2POCH_2CCl_3$	47–48	0.22	1.4596	26.73	26.6	4.49	4.5	11.50	11.60
$(C_2H_5O)_2POCH_2C(CH_3)_3$	51–52	3	1.4187	51.90	52.4	10.17	10.3	14.87	14.86

phite and 0.5 mole (50 g.) of 2,2,2-trifluoroethanol, b.p. 74°, $n^{25}D$ 1.2895, was refluxed (103°) for a period of 8 hr. Because of the closeness of the boiling points of diethyl 2,2,2-trifluoroethyl phosphite, b.p. 48–49° (12 mm.), and unreacted triethyl phosphite, b.p. 52° (12 mm.), only a very small yield of reasonably pure product could be isolated. The mixed alcohol distillate, 34.8 g., $n^{25}D$ 1.3273, consisted, on the basis of its refractive index, of a mixture of approximately equal amounts of ethanol and 2,2,2-trifluoroethanol. Distillation of the reaction mixture *in vacuo* gave 41 g. of material, collected between 45° (10 mm.) and 50° (12 mm.), which refractionated yielded 4.5 g. of diethyl 2,2,2-trifluoroethyl phosphite, b.p. 48–49° (12 mm.), $n^{25}D$ 1.3718.

Anal. Calcd. for $C_6H_{12}F_3O_3P$: C, 32.7; H, 5.5; P, 14.08. Found: C, 33.0; H, 5.5; P, 14.13.

Resolution of 2-Butanol.[18,19]—Phthalic anhydride (4 moles) and 4 moles of 2-butanol were mixed and heated on a steam-bath for 12 hr. The reaction mixture, which solidified on cooling, was dissolved by the addition of strong aqueous alkali. The resulting solution was then adjusted with dilute hydrochloric acid to a weakly basic reaction and extracted three times with ether and the extracted aqueous phase made strongly acidic with hydrochloric acid. The oily product which separated from the solution solidified upon standing overnight. The yield of the crude 2-butyl hydrogen phthalate, m.p. 41–46°, amounted to 99% of the theoretical. The crude ester was recrystallized from ligroin (b.p. 60–90°) to give a yield of 83% of the purified material, m.p. 58–59°, as a white crystal powder.

To 1.5 liters of warm acetone was added with stirring 417.5 g. (1.88 moles) of 2-butyl hydrogen phthalate, m.p. 58–59°, and then 729 g. (1.85 moles) of anhydrous brucine. The resulting solution was maintained at 40° for 1 hour and filtered to remove traces of undissolved material. The filtrate was allowed to stand at room temperature for a period of 16 hr. during which time a white crystalline product separated. By repeated fractional recrystallization from acetone and then from methanol was obtained a final fraction of 405 g. (0.66 mole) of the brucine salt of *d*-2-butyl hydrogen phthalate, m.p. 155–156° (lit.[20] m.p. 154–155°). The mother liquors from the various recrystallizations were combined and evaporated to dryness to leave the semi-solid, crude brucine salt of *l*-2-butyl hydrogen phthalate. Since a satisfactory solvent for the purification of the crude *l*-salt could not be found, the semi-solid material was hydrolyzed without further purification.

The brucine salt of each of the optical isomers was hydrolyzed by the addition of the salt to an aqueous solution containing three equivalents of sodium hydroxide. The mixture was heated and distilled until the refractive index of the distillate remained constant. The aqueous distillate was saturated with potassium carbonate, and the resulting organic layer which separated from the mixture dried with anhydrous potassium carbonate and distilled to yield 0.42 mole of *d*-2-butanol, b.p. 97–98.5°, $n^{25}D$ 1.3941, $[\alpha]^{25}D$ +11.58° (*c* 4.8 in absolute ethanol) (lit.[19] b.p. 99°, $n^{20}D$ 1.3954, $[\alpha]^{20}D$ +13.87°); and 0.56 mole of *l*-2-butanol, b.p. 96.8°, $n^{25}D$ 1.3952, $[\alpha]^{25}D$ −7.85° (*c* 7.3 in absolute ethanol).

Transesterification of *d*-2-Butanol and Triethyl Phosphite.—The transesterification was carried out in the usual manner employing 15 g. (0.2 mole) of *d*-2-butanol and 135 g. (0.8 mole) of triethyl phosphite. The mixture of the reactants was heated for a period of 6 hr. to a final pot temperature of 159°. Fractionation of the reaction mixture yielded 0.105 mole of (*d*)-2-butyl diethyl phosphite, b.p. 68–69° (12 mm.), $n^{25}D$ 1.4167, $[\alpha]^{25}D$ +3.08° (*c* 5.3 in absolute ethanol).

Anal. Calcd. for $C_8H_{19}O_3P$: C, 49.47; H, 9.86; P, 15.95. Found: C, 49.5; H, 10.0; P, 15.91.

Hydrolysis of (*d*)-2-Butyl Diethyl Phosphite.—A solution containing 15 g. of (*d*)-2-butyl diethyl phosphite, $[\alpha]^{25}D$

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(18) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1937 (1913).

(19) M. M. Sprung and E. S. Wallis, THIS JOURNAL, **56**, 1717 (1934).

(20) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

+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°, $n^{25}{}_D$ 1.3713. Using the value $n^{25}{}_D$ 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 $[\alpha]^{25}{}_D$ +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.), $n^{25}{}_D$ 1.4176, $[\alpha]^{25}{}_D$ −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°, $n^{25}{}_D$ 1.3848, containing 80.3% of *l*-2-butanol with a specific rotation of $[\alpha]^{25}{}_D$ −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.), $n^{25}{}_D$ 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, $(C_2H_5O)_2P(O)CCl_2-CH_2OH$, 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.

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ARMY CHEMICAL CENTER, MARYLAND

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

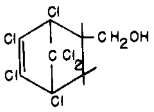
Thiophosphoryl Derivatives of the Adducts from Hexachlorocyclopentadiene and Unsaturated Alcohols

BY ELLIS K. FIELDS

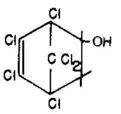
RECEIVED AUGUST 2, 1956

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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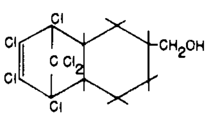

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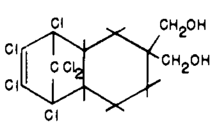
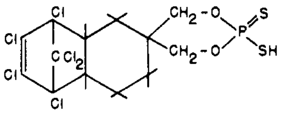
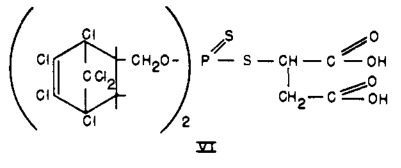


IV

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).