mineral oil (150 ml.) was placed into the flask and heated to 150°. A mixture of 5 ml. of pyridine and 10 g. of phenyl fluoroformate was slowly added. The temperature of the oil bath was increased to 190° and all volatile products were carried over to the cold trap by passing a stream of dry nitrogen through the hot mineral oil. Analysis of the products again showed only trace amounts of fluorobenzene.

D. Boron Trifluoride as a Catalyst.—The same setup as described under A was used. Phenyl fluoroformate (4.5 g.) was placed into the flask and the temperature of the oil bath was increased to 120°. Boron trifluoride was passed through the liquid with a flow rate of 60 cc./min. The product carried over to the cold traps by the BF_3 consisted mainly of unreacted starting material and did not contain any fluorobenzene.

E. Boron Trifluoride Diethyl Etherate as a Catalyst.—The same setup as described under A was used. Freshly prepared BF_3–Et_2O (10 ml.) was placed into the flask, the oil-bath temperature was increased to 50°, and phenyl fluoroformate (5 g.) was slowly added. Then the temperature was increased to 120°. The product, collected in the cold trap, was poured into aqueous NaOH solution and extracted with ether. The ether solution was dried with $MgSO_4$ and checked for fluorobenzene by gas chromatography, but none was found.

Attempted Decarbonylation of Tetrachloroterephthaloyl Difluoride.—The decarbonylation was investigated in the liquid phase without and with catalysts such as BF_3 or AlF_3, and in the gas phase with catalysts such as BF_3, AlF_3, or TiF_4. However, in every case no decarbonylation could be obtained.

The Pyrolysis of *n*-Butyl Phosphate Esters and Salts[1]

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Received March 4, 1965

Separate pyrolyses of tributyl phosphate, dibutyl phosphoric acid, monobutyl phosphoric acid, and barium dibutyl phosphate each produced mixtures of butenes in high yields; barium monobutyl phosphate produced only a 40% yield of the butene mixture, but over 96% of it was butene-1. The extent of isomerization of butene-1 to *cis*- and *trans*-butene-2 varied with the acidity of the ester mixture being pyrolyzed, but the *cis*-to-*trans* ratio from ester pyrolysis remained constant at 0.74 ± 0.02. The composition of the butenes formed from any of the starting materials differed significantly from the thermodynamic equilibrium mixture.

Extensive isomerization of the olefins evolved from the pyrolysis of trialkyl phosphates was observed qualitatively by Baumgarten and Setterquist.[2] In determining the rate constants for the partial pyrolysis of tributyl phosphate (TBP) to form dibutylphosphoric acid (HDBP) and butene-1, we reported[3] that traces of the *cis–trans* isomers of butene-2 were detected after only a few per cent of the TBP had been converted to HDBP. The composition of the gases and liquids formed from the complete pyrolysis of TBP and its degradation products, HDBP and H_2MBP (monobutyl phosphoric acid), was then investigated and is reported here.

It was felt that isomerization would be inhibited if the barium salts of HDBP and H_2MBP [$Ba(DBP)_2$ and BaMBP] were pyrolyzed. Reports published[4] on the pyrolysis of dialkyl phosphates and their zinc salts[4b] and of dialkyl dithiophosphates[4b] and their zinc[4] and lead[4a] salts, however, indicate that much isomerization occurred. In the present study are included the barium salt of HDBP and the singularly acting barium monobutyl phosphate.

Results and Discussion

The composition of the gases obtained from the thermal decomposition of *n*-butyl phosphate esters and salts is shown in Table I. TBP and its acid degradation products, HDBP and H_2MBP, lost on the average over 80% of the butyl groups as butene isomers when heated at 241 to 245°. When TBP decomposed the gas initially evolved was all butene-1, but as the reaction progressed *cis*- and *trans*-butene-2 began to form.[3] More isomerization was found when HDBP decomposed, and the greatest isomerization resulted from the pyrolysis of H_2MBP.

Because the isomerization increased as the reaction mixture became more acid, and because phosphoric acid catalyzes butene isomerization,[5] the pyrolysis was also run with phosphoric acid present initially. A solution of TBP and phosphoric acid in 2:1 mole ratio (equivalent to three HDBP's) decomposed to give results the same as for HDBP. However, thermal decomposition of TBP in the presence of H_3PO_4 was not the only reaction occurring because ester interchange is known to occur more rapidly than thermal decomposition at a lower temperature[6]; the equilibrium mixture from ester interchange probably is established in minutes.

Pyrolysis of the barium salts of dibutyl and monobutyl phosphoric acids gave different results. BaMBP formed nearly pure butene-1; although the butene yield was low (40%), the composition was 98% butene-1 for the 300° product and 96% for that produced at 400–500°. The $Ba(DBP)_2$, however, pyrolyzed to yield 68% of an isomerized gas mixture that contained 60% butene-1, 18% *trans*-butene-2, and 22% *cis*-butene-2. Since *cis*-butene-2 is thermodynamically less stable than *trans*-butene-2, it is surprising to find a higher yield of it than the latter. TBP and the acid esters formed more *trans* than *cis* isomer in all cases. Haag and Pines[7] have shown that the *cis* isomer forms faster than *trans* in the isomerization of butene-1, but at equilibrium its quantity is only about half of that of the *trans* isomer. It therefore appears that the *cis*-to-*trans* conversion rate is radically altered in the case of the $Ba(DBP)_2$ pyrolysis, assuming that butene-1

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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TABLE I

GAS COMPOSITION FROM PYROLYSIS OF *n*-BUTYL PHOSPHATE ESTERS AND SALTS

Compd.	Sample size, mmoles	Temp., °C.	Reaction time, hr.	Yield, %	Isomeric abundance, % Butene-1	Isobutylene	*trans*-Butene-2	*cis*-Butene-2
TBP	1.5–3	242–245	2.25–2.5	77–87	54–55	0.4	25–27	19–20
HDBP	3–5	241–245	0.20–0.25	78–87	34–36	0.7	36–37	26–28
$(TBP)_2 \cdot H_3PO_4$	1[a]	242–244	0.2	80	34	0.7	37	28
H_2MBP	7–9	243–244	0.03–0.07	77–88	18–20	0.8	46–47	33–34
$Ba(DBP)_2$	7	300–470	1.5	67	60		18	22
		300–520	4 addnl.	1	44		27	29
BaMBP	7	300	2.5	8	98		1	1
		400–500	2.5 addnl.	32	96		2	2
		300–680	2 addnl.	7[b]				

[a] Two mmoles of TBP + 1 mmole of H_3PO_4; equivalent to 3 mmoles of HDBP. [b] Decomposed to carbon.

is the gas formed when the C–O bond breaks. If on the other hand the *cis* and *trans* isomers can form directly during the C–O breaking process rather than from subsequent isomerization in the butene-1 formed then the process favors the production of the *cis* isomer.

Isomerization in the butenes from the pyrolysis of $Ba(DBP)_2$ may be due to disproportionation of this salt to form TBP and BaMBP before the butenes evolve. Such a disproportionation reaction for the barium and other salts of diethylphosphoric acid[8] has been reported. TBP has not been isolated from pyrolysis of $Ba(DBP)_2$, but its presence is not ruled out. Pyrolysis of the TBP could then account for the isomerization in the butenes formed.

The stepwise decomposition of TBP (Table II) was done to see when the skeletal rearrangement started to occur. As shown in Tables I and II, very little isobutylene was produced, less than 1% even in the case of H_2MBP where the most isomerization took place. No isobutylene was detected in the first two stages equivalent to the removal of nearly two of three butyl groups. Only in the last 40% of the reaction was it detected to the extent of 0.5%.

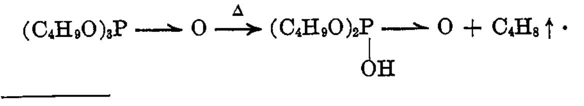
TABLE II

BUTENE COMPOSITION IN STEPWISE TBP DECOMPOSITION[a]

TBP decompn., %	Butene-1,[b] %	Isobutylene, %	*trans*-Butene-2, %	*cis*-Butene-2,[c] %
0–30	91	...	5.2	4
30–60	63	...	22.2	16
60–100	22	0.5	44.5	33

[a] Temperature = 241–244°. [b] Corrected for *cis*-butene-2. [c] Calculated from *cis*-to-*trans* ratio, Table IV.

In the pyrolysis of the butyl phosphate esters the principal products were butenes, but other compounds, predominantly butyl alcohol and dibutyl ether, were obtained in yields of about 15–20%. Table III shows that at the beginning of the TBP pyrolysis dibutyl ether was the main by-product formed; it resulted from the reaction of two TBP molecules to form tetrabutyl pyrophosphate.[3] The butyl alcohol could not form until enough butene had evolved to provide some hydroxyl groups, *i.e.*



$$(C_4H_9O)_3P \longrightarrow O \xrightarrow{\Delta} (C_4H_9O)_2\underset{\displaystyle OH}{\underset{|}{P}} \longrightarrow O + C_4H_8\uparrow \cdot$$

A P–O bond is broken in either butyl ether or butyl alcohol formation. Therefore, when the hydroxy to butoxy group ratio was >1, more butyl alcohol was formed than ether.

TABLE III

COMPOSITION OF ORGANIC LIQUIDS FROM PYROLYSIS OF *n*-BUTYL PHOSPHATE ESTERS AND SALTS

Compd.	Fraction decomposed, %	Temp., °C.	Organic liquid, wt. % Dibutyl ether	Butyl alcohol	Unknown
TBP	15	242–246	89	11	...
	30–70	221	79	20	1
	30–100	221	53	33	14
	0–45	240–245	48	52	...
	45–100	240–245	22	64	14
H_2MBP	100	244	26	74	...
	100	150	13	87	...
	100	178	10	73	17
BaMBP	97	300–500	1	98	1
$Ba(DBP)_2$	100	300–470	0	100[a]	...

[a] Butyl alcohol (76%), water (24%).

The salts pyrolyzed very differently from the esters. The condensable organic liquids were 98 to 100% butyl alcohol. Water was also formed; the chromatogram for the liquid from the $Ba(DBP)_2$ pyrolysis showed 24% water, undoubtedly resulting from the formation of condensed phosphates. Some charring occurred in the reaction flask.

In Table IV the ratios of the butenes produced by pyrolysis are compared with the calculated equilibrium ratios.[9] Only in the case of the pyrolysis of H_2MBP did the composition of the gases approach the equi-

TABLE IV

RATIO OF BUTENE ISOMERS

Compd.	Temp., °C.	*cis*/*trans*	*cis*/1-	*trans*/1-
TBP	243[a]	0.75	0.36	0.48
HDBP	243[a]	0.74	0.77	1.0
$(TBP)_2 \cdot H_3PO_4$	243[a]	0.76	0.82	1.1
H_2MBP	243[a]	0.72	1.8	2.4
$Ba(DBP)_2$	300–470	1.2	0.37	0.30
BaMBP	300	1.0	0.01	0.01
	400–500	1.0	0.02	0.02
Equilibrium[b]	243	0.54	1.90	3.51
	300	0.57	1.50	2.62
	400	0.62	1.11	1.79
	500	0.65	0.86	1.34

[a] Bath temperature ±2°. [b] See ref. 9.

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librium composition, but not with good agreement. Kinetic rather than thermodynamic control apparently determines the product ratios. Kinetic control was proved by Haag and Pines[7] for the isomerization of butenes passed through either alumina or phosphoric acid. Likewise, Hanneman and Porter[4b] have shown that pyrolysis of zinc O,O-di(3-methyl-2-butyl)dithiophosphate at either 215 or 302° had practically no effect on product distribution.

The composite rate of formation of butenes changed radically during the course of the TBP pyrolysis. For samples of the size listed in Table I about 120 min. at 241–245° were required to remove one-third of the butyl groups, an additional 10 min. to remove the next third, and only about 2 min. more for the last third.

Because of the acid catalysis, the ratio of butene-1 to butene-2 isomers decreased considerably during the course of the reaction, but the *cis*-to-*trans* ratio (0.74 ± 0.02) remained constant, within experimental error. HDBP, H_2MBP, and H_3PO_4 were present in varying proportions throughout the reaction; HDBP was generated when the first butene formed, and H_3PO_4 and polyphosphoric acids remained when the reaction was complete. It therefore appears that only the first ionizable hydrogen of the acid catalyst formed had any effect on the group being cleaved, at least as far as *cis* or *trans* isomer formation was concerned.

The mechanism of the production of the butenes is probably ionic in nature. Berti[10] postulated an ionic mechanism for olefin production from the pyrolysis of sulfites. The evolution of alkene from alkyl phosphates is said to be due to formation of a carbonium ion followed by loss of a proton from the β-carbon,[2,4b] presumably to the phosphoryl oxygen.[2] The primary carbonium ion is easily converted by hydride shift[11] to the more stable secondary carbonium ion intermediate which then can produce the *cis*- and *trans*-butene-2.[7,4b]

Once formed the butenes can undergo other reactions before leaving the reaction vessel. Exchange of hydrogens between the butenes and the acids, as observed by Turkevich and Smith,[12] certainly occurs. Isomerization, which is caused by phosphoric acid,[5,7,12] apparently is also caused by HDBP and H_2MBP. All the reactions occurring whereby the butene-2 isomers form must have a similar intermediate, since the *cis*-to-*trans* ratio remains constant through the different stages of TBP decomposition.

Some rearrangement of *n*-butyl groups to *sec*-butyl groups was found in the ester residue left when TBP was 72% decomposed.[13] The amount of rearrangement was small compared to the amount of isomerization of the butenes, however. Evidently, two of the competing reactions are the formation of *cis*- and *trans*-butenes from the secondary carbonium ion and recombination of the secondary carbonium ion with the phosphate anion, with the larger fraction going to butene production.

Experimental

Materials.—The TBP was purified as described earlier.[14] HDBP was prepared by the reaction of 0.3 mole of TBP with 1.5 moles of refluxing ethanolamine.[15] The cooled reaction mixture was transferred to a graduated cylinder with a one-fifth volume water rinse and was extracted twice with fresh ether portions equal to its own volume. Only one-fifth of the excess ethanolamine was removed. The cylinder was therefore chilled in ice and the contents were stirred with a Teflon-coated magnetic stirring bar while sufficient concentrated hydrochloric acid was gradually added to form the $HOCH_2CH_2NH_2 \cdot HCl$ salt. HDBP was removed from this solution in three consecutive ether extractions (equal portions of ether and solution). The ether was removed by means of a rotating evaporator. Any neutral materials in the acid residue were removed by cooling the residue in ice, neutralizing with 4 *M* sodium hydroxide, and extracting three times with a fresh equal volume of ether. Then the HDBP was regenerated by cooling the aqueous solution and gradually adding 0.3 mole of concentrated hydrochloric acid. The HDBP was again extracted in three ether passes. The ether was removed as before; the HDBP, dried at 2 mm., was recovered in 95% yield. Its neutral equivalent was 212 (calcd. 210.2).

H_2MBP was made from Na_2MBP produced by alkaline hydrolysis of butyl dichlorophosphate prepared by the method of Gerrard.[16] To 3.00 moles of aqueous sodium hydroxide (50%) was added dropwise with stirring 0.75 mole of butyl dichlorophosphate, the reaction mixture being kept at 10–15° by cooling in an ice bath. Addition was complete in 2 hr. Complete reaction required an additional 5 hr. with the temperature reaching a maximum of 30°. Neutral materials were extracted from the reaction product with ether. H_2MBP was liberated by the slow addition of concentrated sulfuric acid to the aqueous sodium monobutyl phosphate solution at a temperature of 15–25°. H_2MBP was isolated in 99% yield by continuous ether extraction for 5 hr., followed by removal of the ether and drying *in vacuo*. The product (d^{25}_4 1.225) had a neutral equivalent from alkaline titration of 157 (calcd. 154.1).

Barium monobutyl phosphate and barium dibutylphosphate [BaMBP and $Ba(DBP)_2$] were prepared by neutralization of the free acids with barium hydroxide solution and precipitation of the salts with alcohol addition. BaMBP and $Ba(DBP)_2$ were recrystallized from water–ethanol and 98% ethanol, respectively. Equivalent weights were determined as before[6] and found to be 148 and 279 for BaMBP and $Ba(DBP)_2$, respectively (calcd. 145 and 278).

Pyrolysis.—Small-scale pyrolyses (1.5 to 10 mmoles) were made in a Pyrex test tube (15 mm. o.d. × 16 cm.) fitted with a ball joint. A head with side arm and joint for capillary inlet was clamped to it. The reaction assembly was connected to a 35- or 160-ml. trap, which was connected to a mercury-filled gas buret fitted with a three-way stopcock to allow by-pass or entry. All joints were glass to glass; some were held in place in rubber sleeves. The joints were greased lightly with silicone grease to maintain a leakproof system.

A 50-ml., round-bottomed flask was used for large-scale pyrolyses (50–100 mmoles). The round-bottomed flask was fitted with a helium inlet tube and connected to a trap and gas buret in series. One pyrolysis of 1 kg. of TBP (in a 2-l. round-bottomed flask) was taken to one-third completion by heating 16 hr. at 220°.

A sample of ester or salt, degassed by pumping at 1–2 mm. with the vacuum pump, was weighed into the reaction tube and helium was bubbled through at 5–60 ml./min. until 3–10 l. had passed through the connected system. For 0.5 hr. prior to pyrolysis, the trap was cooled with liquid nitrogen. The flow of helium was stopped and the tubing was closed with a hemostat just above the inlet tube. The system was opened to the gas buret, previously flushed with helium. The capillary inlet tube was broken above the sample surface (so liquid would not run back up the capillary) by moving the ball joint. A heated polyphosphoric acid bath was used to provide temperatures of 150–245°. Higher temperatures for the salts were obtained using a heating mantle and measuring the temperature with a thermocouple and a Tipp-tron automatic thermal control

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(The Tipp Manufacturing Co., Tipp City, Ohio). A slight vacuum was maintained by keeping the mercury leveling bulb a few centimeters below the mercury level in the gas buret. The evolved gases were collected in the liquid nitrogen trap. After cessation of gas evolution the source of heat was removed, mercury in the gas buret was raised to zero, gases in the reaction tube were pumped over to the trap, and the reaction tube was separated without letting air into the trap. With the pyrolytic products frozen in the liquid-nitrogen trap, the helium was removed by evacuating the system to 1 mm. The liquid nitrogen was then removed and the trap was warmed to allow the gases to expand into the gas buret where the volume of gas formed could be measured at ambient temperature and pressure. Per cent yield of butenes then was calculated by converting the volume to STP and comparing with the theoretical volume based on sample weight.

Since the butenes vaporized from their frozen state at different rates, their ratios in the gas buret were not constant. Therefore, the gas were recollected in the trap by applying liquid nitrogen. When the gas volume was not much greater than the volume of the trap (frequently the case when the 160-ml. trap was used), the tubing at the entry and exit tubes were clamped and the trap was removed from the system. When the sample again vaporized, the gases were mixed by shaking with 1 ml. of mercury added prior to pyrolysis. When the volume was large in comparison with the 35-ml. trap, the gases were transferred to a 100-ml., round-bottomed flask fitted with side arm and stopcock and containing 1 ml. of mercury for mixing purposes. A T-tube was connected between the liquid nitrogen trap and the flask. The system was pumped down to 1 mm. and clamped at the T-joint. By cooling the flask in liquid nitrogen while the trap was warmed and opened to the flask, the gases collected in the flask. The flask was removed from the system and warmed to room temperature, and the gases were mixed by shaking with mercury (present in the flask before transfer). A hypodermic syringe was used to collect a sample of the gas for analysis by gas chromatography.

One small-scale (2 mmoles) pyrolysis of TBP was run in increments comprising approximately one-third of total decomposition. The gases collected from each portion were analyzed to determine the extent of isomerization in each stage.

Similarly, large-scale runs (50 to 90 mmoles) were made to determine the composition of the volatile liquids as a function of extent of TBP decomposition. The decomposition products were collected in a Dry Ice trap at 180–250 mm. in a closed system. The extent of decomposition was determined at intervals by stopping the pyrolysis and measuring the volume of gas formed.

Chromatography.—A Perkin-Elmer Model 154 vapor fractometer, equipped with a thermistor-type thermal conductivity detector, was used in the gas–liquid chromatographic analyses. Helium served as the carrier gas. A hypodermic syringe was used to inject the samples (up to 0.5 ml. of gas and up to 0.030 ml. of liquid).

Liquids were analyzed at 100–125° on a 1-m. column of 23 wt. % dinonylphthalate on 30–50-mesh celite. The carrier gas flow was 50 ml./min.

Gases were separated at 20–25° using a 13-ft. column of *o*-nitrophenetole[17] at a flow rate of 50 ml. of helium per minute, or on a 12-ft. column of 29 wt. % of a 1:1 solution of silver nitrate in benzyl cyanide[18,19] on 50–70-mesh celite at a flow rate of 35 ml. of helium per minute. The latter column readily separated the small amount of isobutylene from the main components, and although the butene-1 and *cis*-butene-2 came off as one peak the percentage of isobutylene in the mixture could be easily determined. When a ratio of one weight of silver nitrate to three weights of benzyl cyanide, close to the literature value,[19] was used on 30–50-mesh celite in a 16-ft. column, *trans*-butene-2, butene-1, and *cis*-butene-2 were separated in that order but the small amount of isobutylene present was masked by the large *trans*-butene-2 peak. Ethyl alcohol (50%) was used as the solvent for the silver nitrate–benzyl cyanide solution used in the preparation of the celite column packing. The solvent was removed in the dark at reduced pressure. The dried material was rescreened and packed in 0.25-in. copper tubing 12 ft. in length. The column was coiled to fit in the gas chromatograph.

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Coupling of Naphthalene Nuclei by Lewis Acid Catalyst–Oxidant[1]

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Received April 6, 1965

Naphthalene reacted readily under mild conditions in *o*-dichlorobenzene with ferric chloride–water, aluminum chloride–cupric chloride, and molybdenum pentachloride. With ferric chloride–water, 1,1′-binaphthyl and 1,4-di-α-naphthylnaphthalene comprised the isolable hydrocarbons. In the case of molybdenum pentachloride and aluminum chloride–cupric chloride, the binaphthyl fraction consisted of an isomeric mixture in which the 2,2′ form predominated. Molecular weight data on the crude products indicated an average of about 3–6 naphthalene units per chain. An oxidative cationic mechanism is proposed for the coupling reactions. Apparently the polymerization proceeds *via* coupling in the 1 and 4 positions of the naphthalene monomer. The initially formed products are then subsequently isomerized in those systems containing sufficiently active catalyst.

It was recently shown that aromatic nuclei can be coupled under mild conditions by exposure to Lewis acid catalyst–oxidant, such as ferric chloride,[2] molybdenum pentachloride,[3] or aluminum chloride–cupric chloride.[4] With benzene as the monomer, *p*-polyphenyl was obtained in almost quantitative yield.[5] *p*-Sexiphenyl proved to be the principal product which resulted from either biphenyl or *p*-terphenyl.[6] Studies with ferric chloride revealed the formation of bimesityl from mesitylene,[7] and bixylyls from *m*- and *p*-xylene.[8,9]

Our objective was to investigate the behavior of naphthalene in the system, Lewis acid catalyst–oxidant, and to obtain information concerning the mechanistic aspects. In an earlier paper, brief mention was made of the 1-chloronaphthalene–ferric chloride reaction which yielded a dichlorobinaphthyl (not completely characterized).[10] Before 1900 several investigators reported 1,1′-binaphthyl as a component of the tarry product formed by interaction of naphthalene with

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