

heating in 5 ml of 1 *N* potassium hydroxide in methanol for 3 hr gave 0.22 g (53%) of 5 β -pregnane-3 α ,12 β -diol,⁵ mp and mmp 165–168°.

3-Tetrahydropyranyl Ether of 3 α -Hydroxy-12 β -methanesulfony-5 β -pregnane.—To a chilled (0°) solution of 0.10 g of the 3-tetrahydropyranyl ether of the pregnan-12 β -ol in 2 ml of pyridine was added slowly a chilled solution of 0.20 ml of methanesulfonyl chloride in 2 ml of pyridine. The reaction mixture was allowed to warm slowly to room temperature, and then to stand at room temperature for 18 hr. The pale brown solution was poured into ice water, then extracted with two portions of methylene chloride. The extracts were combined and washed with successive portions of water, dilute hydrochloric acid, and water. After drying the solvent was removed *in vacuo* with gentle warming to yield 0.11 g of pale yellow glass. This material is very unstable, both thermally and in solution, and decomposed on attempted purification. When 0.10 g was treated with potassium *t*-butoxide (from 0.10 g of potassium) in 10 ml of *t*-butyl alcohol, in the manner described for the rearrangement of the rockogenin derivative (see above), there was obtained 0.030 g of pale yellow, nonpolar (eluted with hexane–benzene 2:1 from alumina) material. Tlc (silica gel G) showed that this material was a mixture of two compounds in approximately equal amounts,

and with very similar R_f values. The infrared spectrum did not show the peaks at 6.1 and 11.2 μ associated with a $\Delta^{17a,18}$ olefin.

Registry No.—1b, 15539-07-8; 2a (3-one) (mp 208–210°), 15538-94-0; 2b, 15538-95-1; 3a, 15538-96-2; 3b, 15538-97-3; 4a, 15538-98-4; 4b, 15538-99-5; 5 (17 α -oxide), 15622-67-0; 5 (17 $\alpha\beta$ -oxide), 15539-00-1; 6, 15656-71-0; 7, 4653-71-8; 7 diacetate, 4866-48-2; 3-tetrahydropyranyl ether of 3 β ,17 $\alpha\xi$ -dihydroxy-22a,5 α -D-nor-D-homo-18-norspirostane, 15539-03-4; 3-tetrahydropyranyl ether of 3 β -hydroxy-17 $\alpha\xi$ -amino-22a,5 α -C-nor-D-homo-18-norspirostane, 15539-04-5; 3-tetrahydropyranyl ether of 3 α -hydroxy-5 β -pregnan-12-one, 15539-05-6; 3-tetrahydropyranyl ether of 5 β -pregnane-3 α ,12 β -diol, 15539-06-7; rockogenin-3-tetrahydropyranyl ether 12-methanesulfonate, 11040-86-1.

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The Thermal Decomposition of Tri-*sec*-butyl Phosphate¹

CECIL E. HIGGINS AND WILLIS H. BALDWIN

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

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Organic phosphorus compounds containing *sec*-butyl groups are of practical importance in the solvent extraction technology of uranium.² No information has apparently been published as to their thermal stabilities; it therefore seemed of interest to compare the thermal stability of a secondary isomer with that of its normal counterpart.

The faster thermal dealkylation rate of tri-*sec*-butyl phosphate (TsBP) in comparison with tri-*n*-butyl phosphate (TBP) was qualitatively observed in earlier work.³ Substantially faster thermal decomposition rates have been reported by Emerson, Craig, and Potts⁴ for sulfoxides having both primary and secondary alkyl groups than for those containing only primary groups. A comparison of gaseous products from pyrolysis of the partial esters di-*sec*-butyl phosphoric acid (HDsBP) and di-*n*-butyl phosphoric acid (HDBP) has been made by Hanneman and Porter.⁵ Our work, reported here, compares the thermal decomposition rates of, and isomeric olefin yields from, TsBP with those of TBP.^{6,7}

The composition of butenes produced when TsBP was isothermally decomposed until no more gas evolved is shown in Table I. The reaction was run in the temperature range 180–241°. Very little variation in composition was found: butene-1 comprised 14–17% of the mixture, *trans*-butene-2, 44–48%, and *cis*-butene-2, 38–40%. Only 0.1% isobutylene was formed.

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

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TABLE I

COMPOSITION OF BUTENES FROM COMPLETE PYROLYSIS OF TRI-*sec*-BUTYL PHOSPHATE (TsBP) AT VARIOUS TEMPERATURES

Temp. ±1°	Time, hr	Yield, %	Isomeric abundance, %			
			Butene-1	Iso- butylene	<i>trans</i> - Butene-2	<i>cis</i> - Butene-2
180	6.8	96	13.8	...	48.0	38.2
200	1.4	88	15.6	...	45.2	39.2
212	0.6	90	17.3	...	44.5	37.8
241	0.05	90	15.1	0.1	44.3	40.5

Under similar conditions TBP yielded 54–55% butene-1, 25–26% *trans*-butene-2, 19–20% *cis*-butene-2, and 0.4% isobutylene.⁷ Reaction time was considerably shortened at higher temperatures. At 180° nearly 7 hr were required for complete decomposition (cessation of gas evolution) but at 241° only 2–3 min were required. At this latter temperature, by comparison, TBP took about 2.5 hr to decompose completely.⁷

The composition of the butenes varied greatly from beginning to end of the pyrolysis (Table II). When only 2.5% of the TsBP had decomposed, half of the gas formed was butene-1 and the remainder was distributed between *cis*- and *trans*-butene-2. As the percentage of pyrolytically formed acid in the reaction mixture increased, the amount of butene-1 formed decreased. The last 10% of gas evolved contained only 8.6% butene-1. The latter stage in the pyrolysis was also the only one in which isobutylene was produced (0.2%).

The rates of formation of HDsBP by thermal action on TsBP at several temperatures are shown in Table III. At comparable temperatures the rates are over

TABLE II
 BUTENE COMPOSITION AT VARIOUS STAGES OF TsBP DECOMPOSITION

Decomposn range, ^a %	Temp, ±1°	Heating time, hr	Butene-1	Butene composition		
				Isobutylene	<i>trans</i> -Butene-2	<i>cis</i> -Butene-2
0-2.5	184	2.4	49.1	...	31.5	19.4
0-4	200	0.7	45.8	...	32.9	21.3
0-6	200	0.9	40.1	...	35.4	24.5
0-10	200	1.1	32.3	...	38.9	28.8
0-17	200	1.3	24.9	...	42.6	32.5
0-29	200	1.5	19.3	...	45.8	34.8
0-66	190	3.7	18.0	...	45.7	36.2
0-100 ^b	200	1.4	15.6	...	45.2	39.2
65-82	200	~0.01	8.6	...	48.5	42.4
90-100	208	~0.001	8.6	0.2	50.0	41.2

^a Percentage of total butyl groups. ^b Table I (at 100% decomposition 88% of the butyl groups were recovered as butene isomers).

 TABLE III
 SPECIFIC REACTION RATES FOR THERMALLY INDUCED FORMATION
 OF HDsBP FROM TsBP

Temp, °C	180	190	200	212
$k \times 10^6 \text{ sec}^{-1}$	0.84	1.8	4.1	12

100 times faster than those for the production of HDBP from TBP.⁶ The values found apply only in the early stage of decomposition. Beyond 6-8 mol % HDsBP, acid-catalyzed decomposition became increasingly evident.

Pot residues at various stages of TsBP decomposition were analyzed as previously described³ to see if any rearrangements had occurred in the residual alkyls. TsBP was heated at 190-200° until 13, 68, and 82% of the butyl groups had been eliminated. No rearrangement was detected in the remaining alkyls; the *sec*-butyl groups had not isomerized.

The alkyl groups from the TsBP and its pot residues decomposed to lighter fragments during the HBr dealkylation to a greater extent than the more thermally stable TBP. Where 99.7% pure *n*-butyl bromide was obtained from TBP,³ 97-98% *sec*-butyl bromide was obtained from TsBP. The butyl bromide product from the 82% decomposed TsBP was only 94% pure. Most (4%) of the remainder appeared to be ethyl bromide.

Experimental Section

Materials.—TsBP was prepared by the reaction of purified *sec*-butyl alcohol and phosphorus oxychloride in the presence of pyridine.^{8,9} The product was distilled at 94-97° at 2 mm: d^{25}_4 0.9652; n^{25}_D 1.4175; MR 69.45 (calcd 69.74).

The purity of the *sec*-butyl alcohol used was checked by gas chromatography using a 1-m column of dinonyl phthalate (3

g/10 g of Celite 545, 30-50 mesh) at 110° and a carrier gas flow rate of 50 ml of helium/min. The *sec*-butyl alcohol was 99.6% pure. No butyl groups other than *sec*-butyl were found in the TsBP by the HBr dealkylation method and gas chromatography of the dealkylation products.³ The TsBP was washed with dilute alkali and water and dried *in vacuo* before use.

Pyrolysis.—Rate measurements were made on 0.5-1-g samples (2-4 mmol, dry, acid free, degassed) of TsBP in the temperature range 180-241° (temperatures are corrected). The equipment was the same as described in earlier work.⁷ The bath, preheated to the desired temperature, was raised about the reaction vessel to the same height on all runs. A mercury-filled gas buret and leveling bulb were used for the volume measurements. Rates were obtained by observing the amount of gas (butene isomers) produced as a function of time at a given temperature; values of $\ln [a/(a-x)]$ were plotted against heating time. In the expression $\ln [a/(a-x)]$, a is the initial concentration of TsBP ($a = 1$) and x , the mole fraction converted into HDsBP, was obtained assuming the HDsBP concentration to be equivalent to olefin production in the early stage of decomposition.

A larger sample (6 g, 23 mmol) of TsBP was decomposed 82% at 200° for the purpose of checking the pot residue for possible alkyl isomerization. Dealkylation with 48% HBr was done as before.³

Butene yields from the complete degradation of TsBP until no more gas evolved were high (88-96%). Yields were based on the olefin volume produced, converted into STP, compared with the theoretical volume possible.

Analysis.—Composition of the butenes resulting from pyrolysis of TsBP was detected gas chromatographically. Composition as a function of heating time was determined using a 13-ft column of *o*-nitrophenetole at ambient temperature as previously described.¹⁰ Homogeneous samples of gases resulting from complete decomposition were analyzed using an ice-cooled, 24-ft column of propylene carbonate¹¹ (4 g/10 g of Celite 545, 30-50 mesh) at a helium flow rate of 40 ml/min. This column ensured detection of any isobutylene which might be formed during pyrolysis.

Butyl bromide composition after dealkylation of TsBP, both from starting material and after partial decomposition (13, 68, and 82%), was determined as before³ using the method of Harris and McFadden.¹²

Registry No.—Tri-*sec*-butyl phosphate, 2528-45-2.

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