

grayish slurry was stirred for 1 additional hr. After the ammonia had evaporated, 50 ml. of water was added dropwise. The resulting solution was extracted with ether, and the organic extract was washed with saturated salt solution and dried over sodium sulfate. The ether was removed *in vacuo* to provide 21.2 g. of oil, which vapor phase chromatography indicated to contain 80% of the desired 3,4-diethylpyridine and 13% of 3-ethyl-4-methylpyridine. This product could be purified by fractional distillation (preferably with a 70-plate column) to afford pure 3,4-diethylpyridine, b.p. 208–209°, n_D^{20} 1.5025.

Anal. Calcd. for $C_9H_{12}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.64; H, 9.68; N, 10.08.

More simply, the total product was treated with picric acid, and the crystalline picrate of 3,4-diethylpyridine, m.p. 136–138°, was separated by crystallization from methanol in 50–60% yield. The picrate, on treatment with ammonia, released pure 3,4-diethylpyridine essentially quantitatively.

Isomerization in Residual Alkyls from Pyrolytic and Ester Interchange Reactions of Tributyl Phosphate¹

W. H. BALDWIN AND C. E. HIGGINS

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

Received April 13, 1965

In previous work² considerable isomerization of butenes was observed during the pyrolysis of tri-*n*-butyl phosphate (TBP). The amount of isomerization increased as the acid concentration in the reaction mixture increased. Whether concurrent alkyl group rearrangement took place in the phosphate ester products during pyrolysis was not known.

After finding some rearrangement in the residual alkyl groups from TBP pyrolysis, we wanted to know if rearrangement occurred during ester interchange between TBP and its acid degradation products [dibutyl phosphate (HDBP), monobutyl phosphate (H_2MBP), and H_3PO_4]. The ester interchange reaction occurs at temperatures lower than those necessary for the pyrolytic production of butene.^{2a,3} We also needed to know if ester interchange between TBP and phosphoric acid caused any rearrangement since the method had been used for the preparation of labeled TBP.³ Therefore, TBP to H_3PO_4 ratios and reaction temperatures were chosen at the extremes and intermediate of conditions used in the ester interchange investigation.

The analytical method for determining the alkyl composition in the residues was based on the dealkylation of TBP with other acids.^{4,5} Virtually pure (99.7%) *n*-butyl bromide was isolated by distillation when TBP was heated with constant-boiling HBr. The composition of the mixture of butyl bromide isomers recovered from the residue samples was determined by gas chromatography.

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

(2) (a) C. E. Higgins and W. H. Baldwin, *J. Org. Chem.*, **26**, 846 (1961);

(b) C. E. Higgins and W. H. Baldwin, *ibid.*, **30**, 3173 (1965).

(3) C. E. Higgins and W. H. Baldwin, *ibid.*, **21**, 1156 (1956).

(4) W. H. Baldwin, Chemistry Division Annual Progress Report, Oak Ridge National Laboratory, No. 2782, 1959, p. 40.

(5) A. J. Moffatt and R. D. Thompson, *J. Inorg. Nucl. Chem.*, **16**, 365 (1961).

Results from the ester interchange between TBP and phosphoric acid are listed in Table I. Very little rearrangement occurred within the alkyl groups; the most that was found resulted from the most acid mixture. Only 0.8% of all butyl groups in the reaction products were *sec*-butyl after TBP· H_3PO_4 was heated for 3 hr. at 176°. Under the latter conditions about one-fifth of the butyl groups decomposed into a butene mixture comprised mainly (62%) of *cis*- and *trans*-butene-2. Thus, most isomerization was evident in the gas phase with relatively little observed in the liquid phase.

TABLE I
ISOMERIZATION IN ALKYL GROUPS FROM
TBP- H_3PO_4 ESTER INTERCHANGE

| Mole ratio of TBP to H_3PO_4 | Bath temp. ±1° | Time, hr. | Substance dealkylated | Alkyl composition, % | |
|--------------------------------------|----------------------|--------------|--------------------------|----------------------|-----------------------|
| | | | | <i>n</i> -Butyl | <i>sec</i> - Butyl |
| 1* | 176 | 3 | Pot residue | 99.2 | 0.8 |
| 4 | 177 | 5 | HDBP- H_2MBP | 99.8 | 0.2 |
| | | | TBP | 100 | ... |
| 100 | 206 | 1 | TBP-P ³² | 100 | ... |

* TBP decomposition = 23%.

Labeled TBP is best prepared at TBP to anhydrous, radioactive H_3PO_4 mole ratios of between 40 and 100 to 1 by heating the solution for 1 hr. in a boiling tetralin (206°) bath. Under these conditions, as shown in Table I, no rearrangement occurs. However, when decomposition takes place during the exchange, rearrangement in the esters does occur.

When TBP was pyrolyzed to almost three-fourths completion some isomerization in the ester residue was observed. The results are shown in Table II. Conversion of *n*-butyl groups to *sec*-butyl increased slightly throughout the reaction; about 3% *sec*-butyl was found in the residue from the reaction at 72% decomposition (Table II, column 6). This was about 0.8% yield of *sec*-butyl groups based on the total butyl groups at the start (column 7). Extrapolation of the values in column 7 to 100% reaction indicates that the total *sec*-butyl yield would probably not exceed 1.5%.

The distribution of *sec*-butyl groups in the residue compounds was uniform. TBP, HDBP, and H_2MBP , isolated from the residue, had the same percentage rearrangement, within experimental error, as the residue itself.

The ratios of butene-2 (*cis* + *trans*) and *sec*-butyl yields are shown in column 9, Table II. The ratio doubled over the range 30–72% decomposition; at 72% reaction 23 butene-2 molecules had formed for every *sec*-butyl group left in the residue products. Over this same range the frequency of *sec*-butyl formation increased from one in every 150 C–O scissions to one in every 80–90 (column 10 = per cent TBP decomposed/per cent *sec*-butyl yield). Thus the yield of *sec*-butyl groups increased, but the frequency of formation with respect to butene-2 decreased.

The presence of *sec*-butyl groups in the ester residue products may be due in part to reaction of the acids with dissolved butene product. The electrophilic addition of halogen acids and sulfuric acid to olefins is well known.⁶ Phosphoric acid has been shown by

(6) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 175.

TABLE II
 ISOMERIZATION OF GAS vs. RESIDUE FROM TBP PYROLYSIS

| Pyrolysis temp. $\pm 2^\circ$ | TBP decompn., ^a % | Residual butyls, % | Substance isolated and dealkylated with HBr | Residual alkyl composition, % | | sec-Butyl yield, ^b % | Butene-2 (cis + trans) yield, ^c % | Butene-2/sec-butyl | C-O scissions/sec-butyl |
|-------------------------------|------------------------------|--------------------|---|-------------------------------|-----------|---------------------------------|--|--------------------|-------------------------|
| | | | | n-Butyl | sec-Butyl | | | | |
| 242 | 72 | 28 | Pot residue | 97.2 | 2.8 | 0.78 | 18 | 23 | 92 |
| 221 | 70 | 30 | H ₂ MBP | 97.2 | 2.8 | | | | |
| | | | HDBP | 97.3 | 2.7 | | | | |
| | | | Pot residue | 97.1 | 2.9 | 0.87 | 17 | 20 | 80 |
| 223 | 47 | 53 | Pot residue | 99.2 | 0.8 | 0.4 | 6.9 | 17 | 117 |
| 221 | 30 | 70 | HDBP | 99.6 | 0.4 | | | | |
| | | | TBP | 99.8 | 0.2 | | | | |
| | | | Pot residue | 99.7 | 0.3 | 0.2 | 2.3 | 12 | 150 |

^a All butyl groups removed = 100% decomposition. ^b Based on TBP before pyrolysis. ^c Per cent TBP decomposed $\times 0.82^d \times$ butene-2 fraction. ^d Average yield of butenes from TBP pyrolysis (ref. 2b). ^e Obtained from data in Tables I and II (ref. 2b).

Turkevich and Smith⁷ to exchange hydrogen atoms with olefins; an unstable complex must have formed. The H₃PO₄-catalyzed isomerization of butenes has been explained by Haag and Pines⁸ as the rearrangement of a secondary carbonium ion intermediate to a π -complex, followed by rapid loss of a proton. Since in the pyrolysis of the TBP the butene was being removed from the reaction vessel as it was formed, the chance for recombination was therefore lessened. No butyl ester of phosphoric acid has apparently been isolated from a butene-H₃PO₄ reaction.

Perhaps more rearrangement occurred in the following way. Acid attack on the esters at elevated temperatures caused carbon-oxygen bond fission; the resulting intermediate, whether a primary carbonium ion or a π -complex, could then rearrange to the more stable secondary carbonium ion or π -complex by hydride shift.⁹ Recombination may then have taken place by nucleophilic attack of the acid on the electron-deficient carbon. However, since phosphoric acid esters are weak nucleophiles, the preferred reaction path was proton elimination to give *cis*- or *trans*-butene isomers. The faster dealkylation rate of the *sec*-butyl phosphates in comparison with the *n*-butyl phosphates also hindered the buildup of *sec*-butyl groups in the residue.

Experimental

Ester interchange between TBP and anhydrous H₃PO₄ and recovery of the TBP after reaction were done as before.⁸

TBP was decomposed thermally² to varying extents up to 72%. Individual components were isolated from the pot residues; the acids were neutralized and the TBP was removed by ether or carbon tetrachloride extraction. The aqueous salt solution was cooled in ice and reacidified with concentrated sulfuric acid; H₂MBP and HDBP were then separated by countercurrent batch extraction.¹⁰ The H₂MBP was finally isolated by continuous extraction with ether.

Samples of the products, pot residues, and starting material were dealkylated by refluxing 48% HBr.⁴ A 50-ml., round-bottomed flask served as reaction vessel for 1-5 g. of sample and 10-25 ml. of acid. The butyl bromides formed were distilled through an 11-cm. Vigreux column. Each dealkylation required 0.5 to 0.75 hr. Yields were >95%.

Purity was determined by gas chromatography at 100°. A 1-m. column of 23% dinonyl phthalate (3 g./10 g. of 30-50 mesh Celite) was swept at a flow rate of 50 cc. of helium per minute. The small peak having the retention time common to *sec*-butyl

bromide and isobutyl bromide was found by the method of Harris and McFadden¹¹ to result only from *sec*-butyl bromide. The *sec*-butyl bromide reacted with the silver nitrate at room temperature and no peak was found at the retention time of *sec*-butyl bromide on the 1-m. dinonyl phthalate column in series at 100°. Correction was made for the small amount of isomerization occurring during the dealkylation reaction by running a blank on pure TBP.

(11) W. E. Harris and W. H. McFadden, *Anal. Chem.*, **31**, 114 (1959).

Synthesis of 5- and 6-Methoxyindene¹

J. C. WINTER, D. D. GODSE, AND P. K. GESSNER

Department of Pharmacology,
State University of New York at Buffalo,
Buffalo, New York 14214

Received March 30, 1965

In a study of tautomerism in derivatives of indene, Ingold and Piggott² reported that distillation of either the 5- or the 6-methoxy isomers of 1-indanamine hydrochloride led to the formation of but a single methoxyindene. From this they concluded that indene possesses a mobile tautomeric system. However, Koelsch and Scheiderbauer³ were able to isolate 5- and 6-indenyloxyacetic acids, thus providing the first evidence that the nonbenzenoid double bond of indene occupies a fixed position. Since then, abundant evidence has accumulated,⁴⁻⁷ particularly from the work of Bergson and Weidler,⁸⁻¹¹ that tautomeric forms of monosubstituted indenenes can exist separately. Nonetheless, in the most recently reported attempt to prepare 5-methoxyindene, Panetta and Bunce¹² found that reduction and dehydration of 5- and 6-methoxy-1-indanone led to the same product. They

(1) This work was supported by U. S. Public Health Service Grant 5 R01 MH 07575 and National Institutes of Health Graduate Training Grant 5-T1-GM-107.

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