

ESTER CLEAVAGE BY TRIPHENYLDIBROMOPHOSPHORANE ¹

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The demonstration that triphenyldibromophosphorane is a useful reagent for the cleavage of ethers under essentially neutral conditions² led to the investigation of the behavior of esters with the reagent with the expectation that acid and alkyl bromides would be formed.



The appearance of a brief report of a similar study³ prompts the communication of our results at this time. The data are summarized in the Table. The triphenyldibromophosphorane was prepared as previously described.² It was essential that the apparatus and all reagents be carefully dried.⁴ If the halide products had b.p.s. such as to allow good separation from PhCN, the latter could be used as the solvent. Otherwise, or alternatively, CH₃CN was used as the solvent for reagent formation and then removed (vacuum distillation) before the addition of the ester. Stoichiometric quantities of the reactants were employed with 100 ml. of solvent (PhCN or CH₃CN) for a 0.1 molar reaction. Temperatures of 175-190° were required to complete the reactions in 5-6 hr.,⁵ with the products being removed by distillation as formed. The temperature needed (>230°)² to form bromobenzene from the phenyl esters was not reached.

It seems probable that the ester reacts with triphenyldibromophosphorane to form an oxonium salt which then undergoes cleavage through reaction with

bromide ion. The experiments did not yield information regarding the relative rates of formation of the acid and alkyl bromides in any of the cases studied.

Table *

$\text{RCO}_2\text{R}'$	RCOBr (% yd)	$\text{R}'\text{-Br}$ (% yd)
<u>n</u> -butyl acetate	75.2 ^a 79.5 ^b	74.5 86.0
<u>sec</u> -butyl acetate	86.2 ^a	51.0
<u>n</u> -butyl butyrate	84.8 ^a	52.6
<u>n</u> -butyl propionate	80.5 ^a	84.8
phenyl acetate	48.0 ^a	-
phenyl benzoate	43.1 ^b	-

* Products were identified by comparison (ir, nmr, and vpc) with known samples.

^a PhCN solvent. ^b No solvent.

REFERENCES

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- A. G. Anderson, Jr. and F. J. Freenor, J. Org. Chem., **37**, 626 (1972).
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- Esters were redistilled and stored over Na_2SO_4 or MgSO_4 . Solvents were dried over P_2O_5 or Na_2SO_4 . Bromine was shaken with conc. H_2SO_4 and stored with P_2O_5 . Triphenylphosphine was dried over Drierite in a desiccator. Glassware was flame dried, and a dry N_2 atmosphere was used.
- The use of chlorobenzene (b.p. 132°) as the solvent required much longer (ca. 24 hrs) reaction times and gave lower yields (ca. 34% and 48% of the acid bromide from phenyl acetate and n-butyl acetate, respectively).