our laboratories to elucidate the exact origin of the observed isotope effects and the reason for their variation with nature and concentration of the peroxide.

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Pyrolysis of Esters. I. Nonselectivity in the Direction of Elimination by Pyrolysis

Sir:

We wish to report that published[1] generalizations regarding the direction of elimination on pyrolysis of esters are in grave error. We now find that pyrolysis of secondary acetates gives in appreciable amounts both possible alkenes as well as *cis* and *trans* isomers when such isomerism is possible. Pyrolysis of 1-heptyl acetate (b.p. 186–187°, n_D^{25} 1.4120; lit.[2] b.p. 192.5°, $n_{\text{He (yel.)}}^{15}$ 1.41653) at 540° and a flow rate of 0.6 g. per minute gave pure 1-heptene (b.p. 90–93°, n_D^{25} 1.3962; lit.[3] b.p. 93.5°, n_D^{20} 1.3998) in 56% yield. Homogeneity of this material was established by gas chromatographic analysis using the Wilkins Aerograph equipped with a 5-foot silicone column and with a 10-foot Ucon Polar column. Pyrolysis of 2-heptyl acetate (b.p. 171–173°, n_D^{25} 1.4050; lit.[4] b.p. 71° at 17 mm., n_D^{20} 1.4089) at 485° and a flow rate of 0.67 g. per minute gave a mixture of isomeric heptenes (b.p. 92–98°, n_D^{25} 1.3994; lit.,[5] *trans*-2-heptene, b.p. 97.5–99°, n_D^{24} 1.4056, *cis*-2-heptene, b.p. 98.5–99.5°, n_D^{25} 1.4052) in 84% yield. Gas chromatographic analysis over the 10-foot Ucon Polar column showed 53.9% 1-heptene, 29.3% *trans*-2-heptene (low boiling), and 16.8% *cis*-2-heptene (higher boiling). Above a critical lower temperature, the composition of the pyrolyzate appears to be independent of the temperature and extent of pyrolysis. Thus, pyrolysis of 2-heptyl acetate at 450° and a flow rate of 1 g. per minute gave only 35% of heptenes identical in composition with the product described above.

Pyrolysis of 4-heptyl acetate, which can lead to only one structural isomer without bond rearrangement, on pyrolysis at 485° and flow rate 0.8 g. per minute gave 86% of 3-heptene (b.p. 93–95.5°, n_D^{25} 1.4012; lit.[6] b.p. 95.8–96.1°, n_D^{20} 1.4090). This material was homogeneous to the Ucon chromatographic column except for a small shoulder on the high-retention side of the single peak; this shoulder is interpreted as being due to the presence of a small amount of *cis*-3-heptene, the major component being the *trans*-isomer. Pyrolysis of 3-heptyl acetate at 485° and flow rate 0.6 g. per minute gave a mixture of heptenes (b.p. 91–97°, n_D^{25} 1.4022) in 84% yield. Gas chromatographic analysis over the Ucon column showed 53.5% of 3-heptene, 34.7% of *trans*-2-heptene, and 11.8% of *cis*-2-heptene. The 3-heptene peak showed a shoulder on the high-retention side indicating the presence of a small amount of the *cis*-isomer.

We have also reinvestigated a specific example reported by Bailey and King.[1] Pyrolysis of methylisobutylcarbinyl acetate at 485° and flow rate 0.75 g. per minute gave in 72.2% yield an olefin mixture which on chromatographic analysis over the Ucon column showed two components in the amounts of 44.5% (low retention) and 55.4% (high retention). We assume that the low retention isomer is the lower boiling[7] 4-methyl-1-pentene, while the high retention isomer is the higher boiling[7] 4-methyl-2-pentene.

In view of these results, we must regretfully conclude that the generalizations and the experimental observations of Bailey and associates[1] are in error. We attribute this experimental error to failure of the earlier investigators to utilize precise fractional distillation, thus necessitating the assignment of structure and estimation of homogeneity on infrared analysis alone. Infrared analysis is not an infallible criterion when mixtures are being compared.

We do not wish to generalize our observations at this time. Extensive further investigations are planned.

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[1] W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955); W. J. Bailey, J. J. Hewlitt, and C. King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

[2] R. Bilterys and J. Gisseleire, *Bull. soc. chim. Belg.*, **44**, 576 (1935).

[3] M. L. Sherrill, K. E. Mayer, and G. F. Walter, *J. Am. Chem. Soc.*, **56**, 927 (1934).

[4] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 852 (1914).

[5] B. Gredy, *Bull. soc. chim. Belg.* (5) **2**, 1031 (1935).

[6] F. J. Soday and C. E. Boord, *J. Am. Chem. Soc.*, **55**, 3295, 3300 (1933).

[7] C. G. Schmitt and C. E. Boord, *J. Am. Chem. Soc.*, **54**, 754, 760 (1932).