

## Free-radical Formation in the Reaction of Lead Tetra-acetate with Monocarboxylic Acids

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SEVERAL investigations of the reaction of lead tetra-acetate with monocarboxylic acids have been carried out, but the various authors have arrived at conflicting conclusions as to the reaction mechanism.<sup>1</sup> We have been concerned with the reaction of lead tetra-acetate with aryl, aryl substituted, and bridged polycyclic monocarboxylic acids, and report our results for three particular acids which give, among the major products, compounds whose formation is consistent with free-radical intermediates.

Biphenyl-2-carboxylic acid on reaction with lead tetra-acetate in refluxing benzene gave 3,4-benzocoumarin (the lactone of 2'-hydroxybiphenyl-2-carboxylic acid) in 85% yield.\* The homolytic nature of the intermediate is established by analogy with the work of Kenner, Murray, and

Taylor<sup>2</sup> who found that cyclisation of biphenyl-2-carboxylic acid to 3,4-benzocoumarin occurred in good yield only with homolytic oxidants. Good yields of 3,4-benzocoumarin have also been reported from various reactions of di-*o*-phenylbenzoyl peroxide.<sup>2-5</sup> Moore and Arzoumanian<sup>6</sup> reported the conversion of diphenic acid into 3,4-benzocoumarin by reaction of lead tetra-acetate in refluxing pyridine-acetonitrile, but that reaction, as suggested by the authors, is almost certainly ionic.  $\delta$ -Phenylvaleric acid, on heating under reflux in benzene solution with lead tetra-acetate, gave *n*-butylbenzene (4%) and tetralin (54%); in cyclohexane, *n*-butylbenzene (10%) and tetralin (50%) were obtained. These products are formed, though in varying amounts, in other well-authenticated reactions involving the radical

\* Yields based on moles per mole of lead tetra-acetate.

<sup>1</sup> M. S. Kharasch, H. N. Friedlander, and W. H. Urry, *J. Org. Chem.*, 1951, **16**, 533; W. A. Moscher and C. L. Kehr, *J. Amer. Chem. Soc.*, 1953, **75**, 3172; E. J. Corey and J. Casanova Jr., *J. Amer. Chem. Soc.*, 1963, **85**, 165; W. H. Starnes, Jr., *J. Amer. Chem. Soc.*, 1964, **86**, 5603; D. Benson, L. H. Sutcliffe, and J. Walkley, *J. Amer. Chem. Soc.*, 1959, **81**, 4488.

<sup>2</sup> G. W. Kenner, M. A. Murray, and C. M. B. Taylor, *Tetrahedron*, 1957, **1**, 259.

<sup>3</sup> J. K. Kochi and R. D. Gilliom, *J. Amer. Chem. Soc.*, 1964, **86**, 5251.

<sup>4</sup> F. D. Green, G. R. van Norman, J. C. Cantrill, and R. D. Gilliom, *J. Org. Chem.*, 1960, **25**, 1790.

<sup>5</sup> D. B. Denney and P. P. Klemchuk, *J. Amer. Chem. Soc.*, 1958, **80**, 3289.

<sup>6</sup> W. R. Moore and H. Arzoumanian, *J. Org. Chem.*, 1962, **27**, 4667.

$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot$ .<sup>3,7,8</sup> The high yield of tetralin in our reaction indicates that it could be of synthetic importance in related systems. Apocamphane-1-carboxylic acid<sup>9</sup> reacted with lead tetra-acetate in refluxing benzene to give 1-phenylapocamphane (56%). In view of the reluctance of bridgehead carbonium ions to form, this reaction is consistent with the intermediacy of the 1-apocamphyl radical. This intermediate is presumably also involved in the photochemical

conversion of the acyl hypiodite of apocamphane-1-carboxylic acid into 1-iodoapocamphane.<sup>10</sup>

As a result of a recent study of the reaction of lead tetra-acetate with aliphatic monocarboxylic acids, Kochi<sup>11</sup> has put forward a free-radical chain mechanism on the basis of inhibition of the reaction by oxygen and catalysis by copper salts. However the nature of the products formed was not so generally meaningful as in our examples.

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<sup>7</sup> D. F. DeTar and C. Weis, *J. Amer. Chem. Soc.*, 1956, **78**, 4296.

<sup>8</sup> P. J. Bunyan and D. H. Hey, *J. Chem. Soc.*, 1962, 1360.

<sup>9</sup> P. D. Bartlett and L. H. Knox, *J. Amer. Chem. Soc.*, 1939, **61**, 3184.

<sup>10</sup> D. H. R. Barton, H. P. Faro, E. P. Serebryakov, and N. F. Woolsey, *J. Chem. Soc.*, 1965, 2438.

<sup>11</sup> J. K. Kochi, *J. Amer. Chem. Soc.*, 1965, **87**, 1811.