The Mechanism of Friedel–Crafts Alkylations by Lactones

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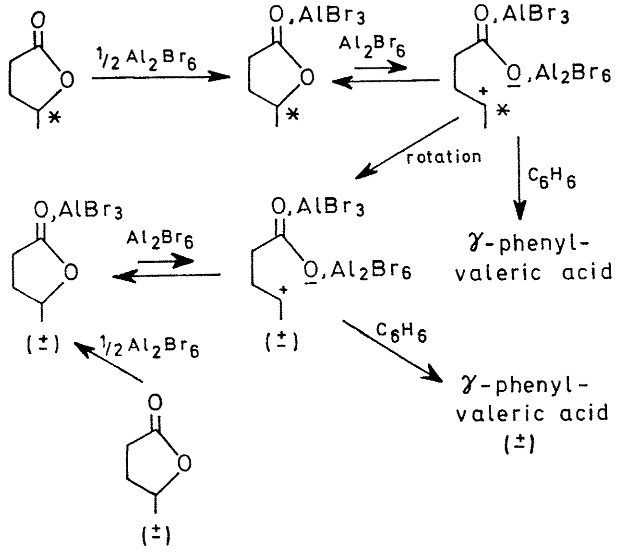
Summary The alkylation of benzene by γ-valerolactone catalysed by aluminium bromide in 1,2,4-trichlorobenzene solvent has a rate law: $r = k[\text{benzene}][\text{lactone}][Al_2Br_6 - (\text{lactone})_0/2]$ where $k = 0{\cdot}61\ \text{M}^{-2}\,\text{s}^{-1}$ at 35°.

FRIEDEL–CRAFTS alkylations are widely used synthetically and have been studied extensively,[1] but detailed kinetic and mechanistic studies have been rather limited and difficult to interpret.[2] With the recent discovery of some stereospecific Friedel–Crafts reactions,[3,4] which allowed more detailed mechanistic speculation, it has become important to explore the kinetics of alkylations by lactones. We report a study of the kinetics of the alkylation of benzene by γ-valerolactone in 1,2,4-trichlorobenzene solvent catalysed by aluminium bromide, a homogeneous system. The reaction was followed by n.m.r. spectrometry, and the data were found to be fit best by the rate law:

$$-\mathrm{d}(\text{lactone})/\mathrm{d}t = k[\text{benzene}][\text{lactone}][Al_2Br_6 - (\text{lactone})_0/2]$$

where $k = 0{\cdot}61\ \text{M}^{-2}\,\text{s}^{-1}$ at 35° and $(\text{lactone})_0$ is the initial lactone concentration. In order to interpret the kinetics properly it was necessary to ascertain the state of aggregation of the aluminium bromide under the reaction conditions; freezing point depression measurements showed it to be dimeric (Al_2Br_6).



SCHEME

* Indicates optically active materials.
(±) Indicates racemic materials.

This rather unusual rate law indicates the presence of three atoms of aluminium in the activated complex. It is probably best interpreted in terms of (i) essentially irreversible complex formation to give lactone, $AlBr_3$, the complex itself being incapable of reaction, followed by (ii) reaction with Al_2Br_6 to form ultimately an ion pair which is capable of return to the previous complex, bond rotation, and (iii) alkylation by an aromatic compound to produce an acid complexed with monomeric aluminium bromide. In accord with this description, no reaction occurs unless Al_2Br_6 is present in an excess of over one-half of the initial lactone concentration.

The kinetics of racemization of optically active lactone were also examined and were shown to fit a rate law with the same dependence upon aluminium bromide as that for alkylation. The apparent rate constant is different since rate-determining step is different, but rate laws and rate constants for both reactions are consistent with our previous stereochemical studies[3a] in which relative rates of return, rotation, and alkylation by an intermediate ion pair were deduced. A simple mechanism consistent with our observed kinetics and stereochemistry is given in the Scheme.

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[1] G. A. Olah, ed., 'Friedel-Crafts and Related Reactions,' Interscience, New York, 1963.

[2] H. C. Brown and M. Grayson, *J. Amer. Chem. Soc.*, 1953, **75**, 6285; H. Jungk, C. R. Smoot, and H. C. Brown, *ibid.*, 1956, **78**, 2185; C. R. Smoot and H. C. Brown, *ibid.*, p. 6245.

[3] (a) J. I. Brauman and A. J. Pandell, *J. Amer. Chem. Soc.*, 1967, **89**, 5421; (b) J. I. Brauman and A. Solladié-Cavallo, *Chem. Comm.*, 1968, 1124.

[4] T. Nakajima, S. Suga, T. Sugita, and K. Ichikawa, *Tetrahedron*, 1969, **25**, 1807; S. Suga, T. Nakajima, Y. Nakamoto, and K. Matsumoto, *Tetrahedron Letters*, 1969, 3283; T. Nakajima, S. Suga, T. Sugita, and K. Ichikawa, *Bull. Chem. Soc. Japan*, 1967, **40**, 2980.