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A NEW AND EASIER ROUTE TO TETRONIC ACID

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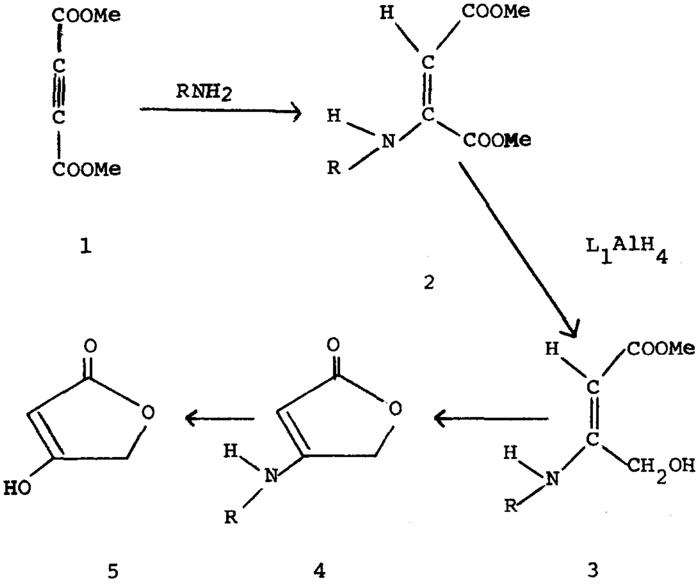
The published methods[1,2] for the preparation of tetronic acid (5) give poor yields and we have found some of them difficult to repeat. In carrying out reductions on compounds containing the enaminone system[2] it seemed that the enaminone double bond and carbonyl group were more difficult to reduce than a comparable conjugated enone. This prompted us to investigate the route shown overleaf. The idea was that the carbonyl group involved in the enaminone (vinylogous urethane) system would not be reduced as readily as the ester carbonyl and that the resulting alcohol (3) could be induced to cyclise fairly readily.

Reduction of compound 2, R = Me, Bu^t or Ph with $LiAlH_4$ led directly to the cyclic enaminone (4) and no intermediate alcohol (3) has been isolated.

The final stage, involving hydrolysis[2] of the enaminone (4) was followed by u.v. spectrophotometry and gave essentially pure tetronic acid (5) m.p. 140° (lit.[1] m.p. 140-142°), i.r., n.m.r., u.v. and mass spectra were all consistent with the required structure.



The overall yield from dimethylacetylene dicarboxylate was 30% which compares well with other methods[1] and we find this route easier and simpler to carry out than any previously published.

1. L.J. Haynes and J.R. Plimmer, Quarterly Reviews, 1960, 14, 292;
T.P.C. Mulholland, R. Foster and D.B. Haydock, J. Chem. Soc. (Perkin I), 1972, 1225.

2. K. Dixon and J.V. Greenhill, J. Chem. Soc., (Perkin II), 1974, 165.