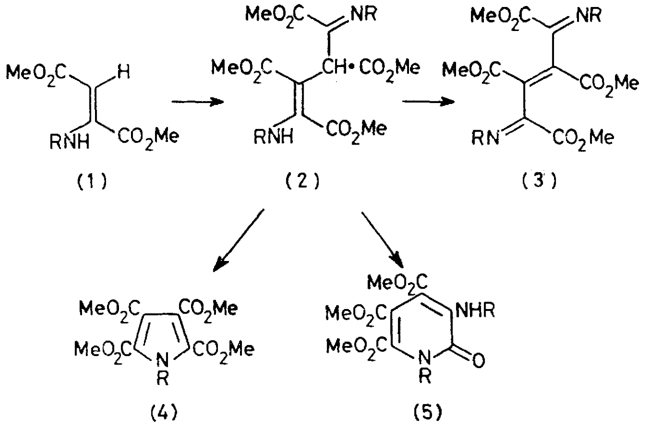
Heterocyclic Products from the Oxidation of *N*-Alkylaminofumarates

By RICHARD M. CARR, RICHARD O. C. NORMAN, and JOHN M. VERNON*
(*Department of Chemistry, University of York, Heslington, York* YO1 5DD)

Summary The five types of product available from oxidation of dimethyl *N*-alkylaminofumarates with lead tetraacetate include new polyester derivatives of pyridine, pyrrole, and pyrrolo[3,2-*b*]pyrrole ring systems.

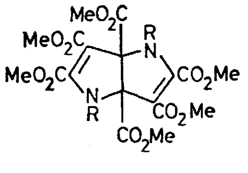
LEAD tetra-acetate (LTA) is an important and versatile oxidant for organic compounds.[1] A brief report[2] of the oxidation of dimethyl anilinofumarate (**1**; R = Ph) with LTA to give the *N*-phenylpyrroletetraester (**4**; R = Ph) prompted our investigation of similar oxidations of *N*-alkylaminofumarates. Oxidation with LTA of other simpler enamines has been reported,[3] and does not give rise to heterocyclic products. We have obtained so far five types of product from a series of *N*-alkylaminofumarates (**1**).

Conjugated enedi-imines (**3**; R = $\mathrm{Pr^i}$, cyclo-C_6H_{11}, or $\mathrm{Bu^t}$)† with the stereochemistry shown are obtained (*ca.* 25% yield) from (**1**; R = $\mathrm{Pr^i}$, cyclo-C_6H_{11}, or $\mathrm{Bu^t}$) with an equimolar amount of LTA in dichloromethane at room temperature. With less LTA the intermediates (**2**; R = $\mathrm{Pr^i}$ or cyclo-C_6H_{11}) are isolable. Alternatively, compound (**2**; R = $\mathrm{Bu^t}$) was obtained by catalytic hydrogenation of (**3**; R = $\mathrm{Bu^t}$), and the intermediates (**2**), separately treated with LTA, were converted into the end-products (**3**). Both (**2**) and (**3**) are oxidative dimers of the enamines (**1**) coupled through the β-carbon atom.



SCHEME

The other three types of product are the heterocycles (**4**)—(**6**), mixtures of which are formed (up to 60% yield) by LTA-oxidation of (**1**; R = Me or Et) in dichloromethane containing trifluoroacetic acid. The products (**4**) and (**5**) are probably derived from the same intermediate (**2**) (Scheme), since compound (**2**; R = $\mathrm{Pr^i}$) was independently cyclised to the corresponding pyrrole (**4**; R = $\mathrm{Pr^i}$) or pyridinone (**5**; R = $\mathrm{Pr^i}$) in acidic or basic conditions, respectively. According to precedents,[4] either acid or base would also catalyse the necessary change in stereochemistry of the enamine unit of structure (**2**). Alternatively, the pyrrole (**4**; R = Me), which is the least abundant component of the mixed products (**4**)—(**6**), is obtained directly and in better yield (27%) from (**1**; R = Me) and LTA in refluxing acetonitrile.



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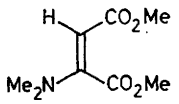

(7)

The last type of LTA-oxidation product, for which we suggest the pyrrolo[3,2-*b*]pyrrole structure (**6**), is the most unusual. The symmetry of this structure is reflected in ^1H and ^{13}C n.m.r. spectra, and other evidence includes the notable similarity of the u.v. spectrum and some ^{13}C chemical shifts of (**6**; R = Me) with those of dimethyl *NN*-dimethylaminomaleate (**7**). Clearly three molecules of (**1**) are required for the formation of one of (**6**), but further work is required to define the mechanism for this reaction and to develop other possibilities of heterocyclic synthesis.

(*Received*, 25*th August* 1977; *Com.* 903.)

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† Satisfactory microanalyses were obtained for all new compounds.

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[2] S. K. Khetan, *J.C.S. Chem. Comm.*, 1972, 917.

[3] F. Corbani, B. Rindone, and C. Scolastico, *Tetrahedron*, 1973, **29**, 3253; 1975, **31**, 455.

[4] *Cf.* K. Herbig, R. Huisgen, and H. Huber, *Chem. Ber.*, 1966, **99**, 2546.