

THE ACTION OF SECONDARY AMINES ON MYOINOSITOL HEXANITRATE.
THE FORMATION OF DIALKYLAMMONIUM CROCONATES.

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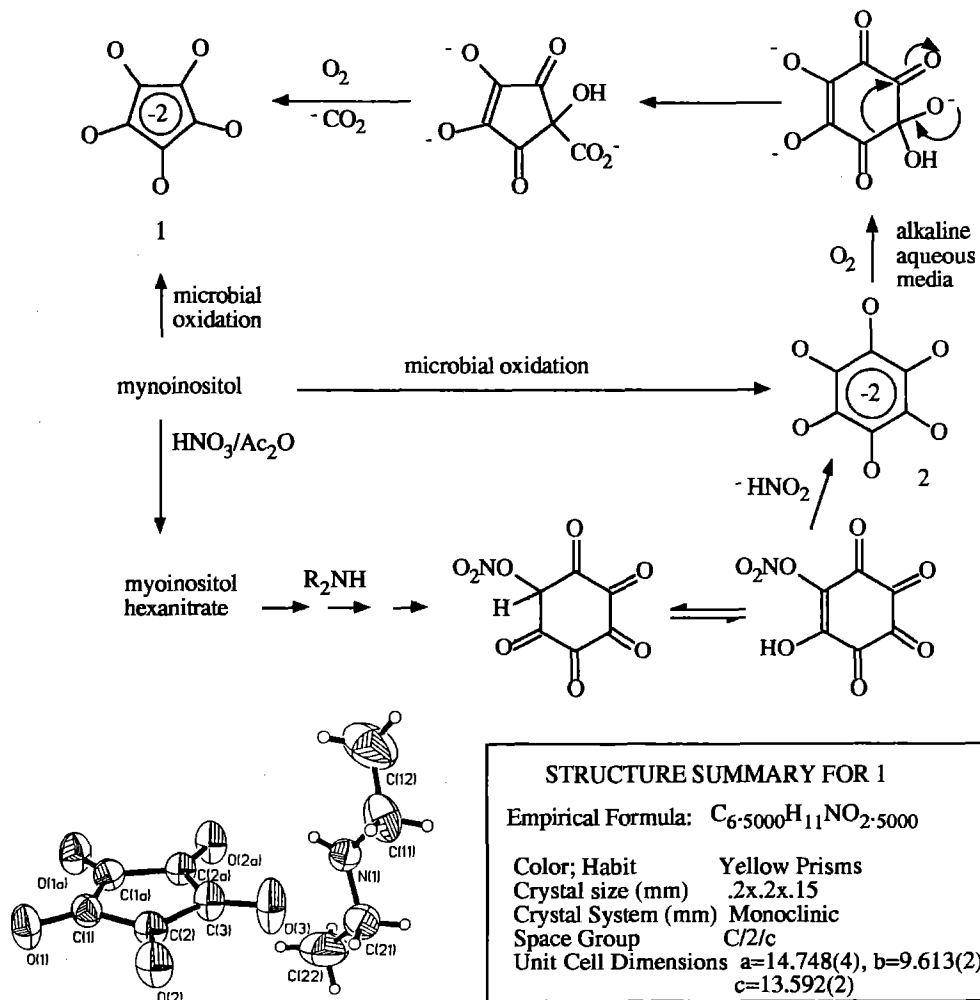
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Abstract: *Treatment of myoinositol hexanitrate with secondary amines yields croconates. This is a new synthetic route to these interesting aromatic anions.*

We have found that treatment of myoinositol hexanitrate with diethylamine in methanol at -10°C results in the formation of diethylammonium croconate, **1**. This is an unusual and interesting synthesis of croconate anion, which previously could only be prepared by bubbling oxygen through an alkaline solution of rhodizonate, **2** (1). The latter can be prepared by microbial oxidation of myoinositol or by reaction of potassium with carbon monoxide (2,3).

The formation of croconate from rhodizonate occurs via an interesting ring contraction, an example of an oxo alcohol rearrangement related to the benzilic acid rearrangement (4). West, in his monograph on Oxocarbons (4), notes that this is the only route which has been developed for the preparation of croconates. Our observations that simple nitration of myoinositol with fuming nitric acid in acetic anhydride, followed by treatment of the hexanitrate with amine (both diethylamine and piperidine work quite well), provides another useful route to this interesting class of compounds. This route may in fact occur through **2**, which could arise from the hexanitrate through the sequential elimination of HNO_2 .

There have been no previous reports of x-ray structures of dialkylammonium croconates, though the ammonium salts have been studied by x-ray crystallography (5). In order to establish the structure of **1** unequivocally we have carried out a single crystal x-ray analysis of this yellow-orange product. The structure was found to refine smoothly in the centric space group C2/c . Refinement in the noncentric group Cc resulted in unreasonable thermal parameters and standard deviations in atomic positions. While the croconate ion was well behaved in refinement, considerable disorder was observed in the diethylammonium cation. Data collection parameters and structural results are summarized alongside the structure. Bond lengths and angles in croconate ion agree with those previously determined (5).



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