# Substituted Butyrolactones from Ylidenemalononitriles

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WHEN α-cyano-β-isopropylcinnamonitrile (I; $R^1$=Ph; $R^2$=$R^3$=Me) was treated with polyphosphoric acid, a lactone (II; $R^1$=Ph; $R^2$=$R^3$=Me) was the principal product. This result was unexpected, since concentrated sulphuric acid had converted this and related ylidenemalononitriles into a mixture of indanones and indenones.[1] A careful examination of the mother liquors of the product of sulphuric acid cyclization of (I; $R^1$=Ph; $R^2$=$R^3$=Me) revealed that (II; $R^1$=Ph; $R^2$=$R^3$=Me) (5—10%) had been formed in this reaction also. No aromatic ketones were observed in the polyphosphoric acid cyclization of (I; $R^1$=Ph; $R^2$=$R^3$=Me).

While conversion of unsaturated acids into lactones, with double bond migration, is common,[2] few examples of the formation of lactones directly from unsaturated nitriles have been reported,[3,4] and these have not involved migration of the double bond. In order to determine the general utility of this reaction as a synthetic tool, additional ylidenemalononitriles (see Table) were treated with polyphosphoric acid under the same reaction conditions. The results of these experiments are shown in the Table.

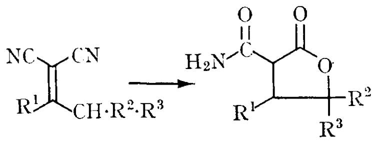
TABLE

| $R^1$ | $R^2$ | $R^3$ | Yield of (IV) (%) |
|---|---|---|---|
| Ph | Me | Me | 86 |
| $Me_2CH$ | Me | Me | 61 |
| H | Me | Me | 27 |
| Ph | $-[CH_2]_5-$ | | 83[a] |

[a] Spirolactone formed.

The present report therefore represents a convenient new synthesis of γγ-disubstituted lactones, of interest in the natural products field.[5] Furthermore, this general procedure usually produces better yields of γγ-disubstituted lactones than the previously reported procedure which involves levulinate esters and Grignard reagents.[5] It should be noted that cold concentrated sulphuric acid usually converts unsaturated acids into lactones, due to its strong ability to protonate the ethylene linkage, while hot polyphosphoric acid usually produces ketones due to preferential attack of the carbonyl group producing either acylium ions or polarized complexes,[2] just the reverse of the results observed with (I; $R^1$=Ph; $R^2$=$R^3$=Me).

The general method for the synthesis of these lactones involves treatment of the ylidenemalononitrile in ten times its weight of polyphosphoric acid at 100° for 12 hours, followed by hydrolysis in a tenfold excess of water. The solids are isolated by filtration while the water-soluble lactones are extracted with chloroform.



(I) (II)

All the lactones (II) have been identified by elemental analysis, spectral data[*], and characteristic reactions.

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[*] Nuclear magnetic resonance spectra were run on a Varian model A-60 with tetramethylsilane used as an internal standard.