Cyclic Thioanhydrides: Potentially Versatile Functional-groups in Organic Synthesis

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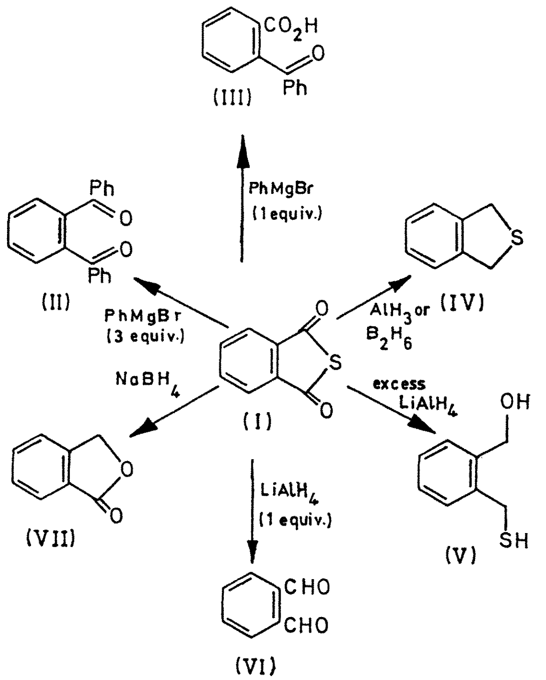
Summary Some simple high-yield conversions of a cyclic thioanhydride into a diketone, keto-acid, sulphide, alcohol-thiol, dialdehyde, and lactone are described.

SINCE development of new and versatile functional-groups is an important aspect of organic synthesis, we have studied cyclic thioanhydrides, a little-understood class of organo-sulphur compounds. We report some novel reactions of thiophthalic anhydride (I)[1] with phenylmagnesium bromide and metal hydrides. These results suggest that cyclic thioanhydrides may be potentially useful synthetic intermediates.

Although cyclic thioanhydrides are readily prepared either from their corresponding diacids or anhydrides, the reaction of these compounds with organometallic and metal hydride reagents has not been reported to our knowledge. When an ethereal solution of (I) was treated with 3 equiv. of phenylmagnesium bromide, followed by acid hydrolysis, a mixture of *o*-dibenzoylbenzene (II),[2] diphenylisobenzofuran,[3] and diphenylisobenzothiophen,[3] was formed. A variety of experimental conditions were examined to improve the overall yield of (II) from (I). It was found that oxidative hydrolysis of the reaction mixture using Brown's procedure[4] gave only the diketone in greater than 80% yield. Phenyl-lithium also gave the same result but in somewhat lower yield. The only comparably direct procedure for the preparation of (II) is the reaction of phthaloyl chloride at −55° with phenylmagnesium bromide (32% yield).[5]



The addition of one phenyl group to (I) is also possible with the Grignard reagent. Treatment of the thioanhydride with 1 equiv. of phenylmagnesium bromide followed by oxidative work-up gave the keto-acid (III) in 50% yield. The formation of keto-acids from cyclic anhydrides and phenylcadmium occurs in somewhat better yield but is experimentally cumbersome relative to the thioanhydride procedure.[6]

Reduction of (I) with either aluminium hydride or diborane smoothly gave the sulphide 1,3-dihydrobenzo[*c*]-thiophen (IV) in nearly quantitative yield. Cava and co-workers report a 43% yield of (IV) from α,α′-dibromo-*o*-xylene.[7] Treatment of the thioanhydride with an excess of lithium aluminium hydride gave rise to the alcohol-thiol (V).[8] In marked contrast, reduction of the thioanhydride with one mole of $LiAlH_4$ gave *o*-phthalaldehyde (VI) in yields varying from 50 to 70%. A benzene–methanol solution of (I) on reaction with sodium borohydride gave rise to phthalide (VII) in 80% yield.

While no attempt has been made to maximize product formation in the above reactions, the transformations of (I) leading to (II)—(VII) occur in yields comparable or superior to other methods used for the preparation of these materials.

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