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THE FORMATION OF ACYL ANHYDRIDES COUPLED TO THE REDUCTION OF A QUINOIDAL SYSTEM

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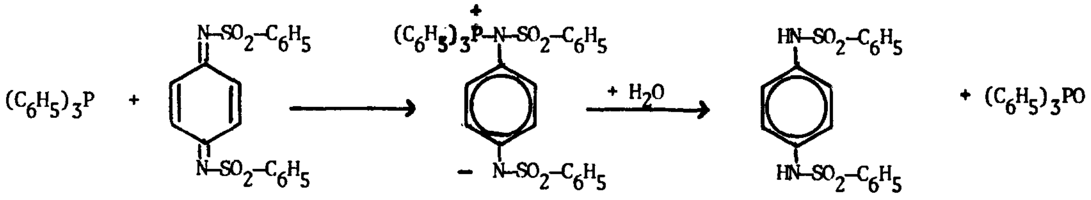
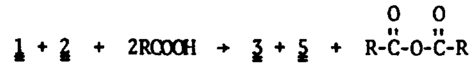
In a recent paper[2] Mustafa et al. reported the reaction of triphenylphosphine (1) with p-benzoquinonedibenzenesulfonimide (2) in a dry benzene solution to yield a violet colored precipitate. Upon exposure to the atmosphere, the color of the precipitate faded and triphenylphosphine oxide (3) was isolated from the reaction mixture. Though not quoted by the Egyptian authors, this observation had already been reported some thirteen years earlier by Horner and Klupfel.[3] The latter suggested structure 4 for the colored intermediate and identified the other product of its reaction with water (moisture) as p-phenylenedibenzenesulfonamide (5). The work of Ramirez et al.[4] showed that the colored, free radical intermediates produced in the formally similar reaction of triphenylphosphine with p-benzoquinone



1 2 4 5 3

Eq. 1

result from rather complex interactions. It is therefore questionable whether the violet color (which we find to be produced subsequent to a blue color) is correctly attributable to structure **4**. Nonetheless, it is at least plausible that the intermediate which reacts with water may have this structure. Irrespective of mechanistic considerations, the overall stochiometry of Eq. 1 suggested that an equimolar mixture of **1** and **2** might serve as a dehydrating agent as, for example, in the conversion of carboxylic acids to their anhydrides (see Eq. 2).



$$\mathbf{1} + \mathbf{2} + 2RCOOH \rightarrow \mathbf{3} + \mathbf{5} + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$$

Eq. 2

The success of such a reaction would be of topical interest as it involves the conversion of the "oxidative energy" of a quinoidal system into the "acylative energy" of an anhydride (cf. Ref.5) and references quoted therein). Oxidative phosphorylation as well as other important biochemical reaction sequences, involve similar conversions.

We now report the achievement of the reaction outlined in Eq. 2.

General Method: A solution of **2** (30 mmole) in dry benzene was added with stirring and under a dry nitrogen atmosphere, to a dry benzene solution containing 30 mmole of **1** and 60 mmole of the carboxylic acid. The reaction mixture turned blue and then colorless again, and a white precipitate appeared. After one-half hour at ambient temperatures, the precipitate was removed by filtration and its identity as **5** was confirmed by m.p. and i.r. spectrum. The solvent was removed from the filtrate under reduced pressure. The residue contained **3**, remains of **5**, and the carboxylic anhydride. The latter was recovered in most cases by vacuum distillation. It may also be isolated by chromatography on specially dried silica gel.[6] Pure mesitoic anhydride was obtained by treating the crude residue with ethanol in which the byproducts are soluble, and the anhydride relatively insoluble. The identities of the anhydrides were confirmed by determination of m.p. or b.p., by spectral means, and by conversion to the known anilides. Yields of isolated anhydrides were:mesitoic anhydride, 75%; benzoic anhydride, 65%; pivalic anhydride, >90%; butyric anhydride, 50%.

It will be noted that the method is applicable to both aliphatic and aromatic carboxylic acids, with unhindered or hindered carbonyl groups. The high yields of pivalic and mesitoic anhydrides, as well as spectral data on crude reaction products, suggest that the lower yields of anhydrides with unhindered carbonyls are primarily due to their more extensive hydrolysis during isolation.

In parallel exploratory experiments, using p-benzoquinonedimethanesulfonimide, we found, not unexpectedly, that it also reacts with **1** in dry benzene to yield a blue-violet color and precipitate, and that upon addition of water the color is discharged and p-phenylenedimethanesulfonamide is formed. Likewise, reaction of carboxylic acids with p-benzoquinomedimethanesulfonimide and **1** yields carboxylic anhydrides.

Next, the synthesis of an ester by the reaction of equimolar quantities of **1**, **2** and benzoic acid in benzene solution containing a large excess of methanol, was attempted. Methyl benzoate was isolated, but only in ca. 50% yield. Similarly, the reaction of equimolar amounts of **1**, **2** and benzoic acid in benzene solution with a 60% excess of aniline produced the expected amide, benzanilide, but in only 33% yield. These relatively low yields of ester and amide preclude a conclusion as to whether they were formed by the reaction of the alcohol and amine, respectively, with an intermediate, as yet unidentified, phosphorous containing acylating species, or by their reaction with first formed benzoic anhydride.

In the reaction of equimolar amounts of **1** and **2** in benzene solution with two equivalents of n-butanol or cyclohexanol, the disappearance of the blue-violet color was slower. Nevertheless, the reduction of the disulfonimide and the oxidation of the triphenylphosphine did occur. The alphatic alcohols were not converted to ethers, (contrast to behavior of carboxylic acids) but dehydration, at least in part, to an olefinic fraction was noted. It is also likely that reductive alkylation of **2** occurred, since in a similar experiment with methanol we obtained chromatographic evidence for the formation of N-methylated *p*-phenylenedibenzenesulfonamide.

A method for the preparation of anhydrides, formally related to the one described herein, and involving the reaction of tri-*n*-butylphosphine with carboxylic acids in the presence of organo-mercury compounds, has been described by T. Mukaiyamo.[7]

A number of mechanisms, some involving intermediate **4**, may be postulated for the reaction sequence yielding anhydrides. A decision between them must await further work.

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