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TRANSITION METAL MEDIATED ELIMINATIONS IN ANHYDRIDES AND THIOANHYDRIDES

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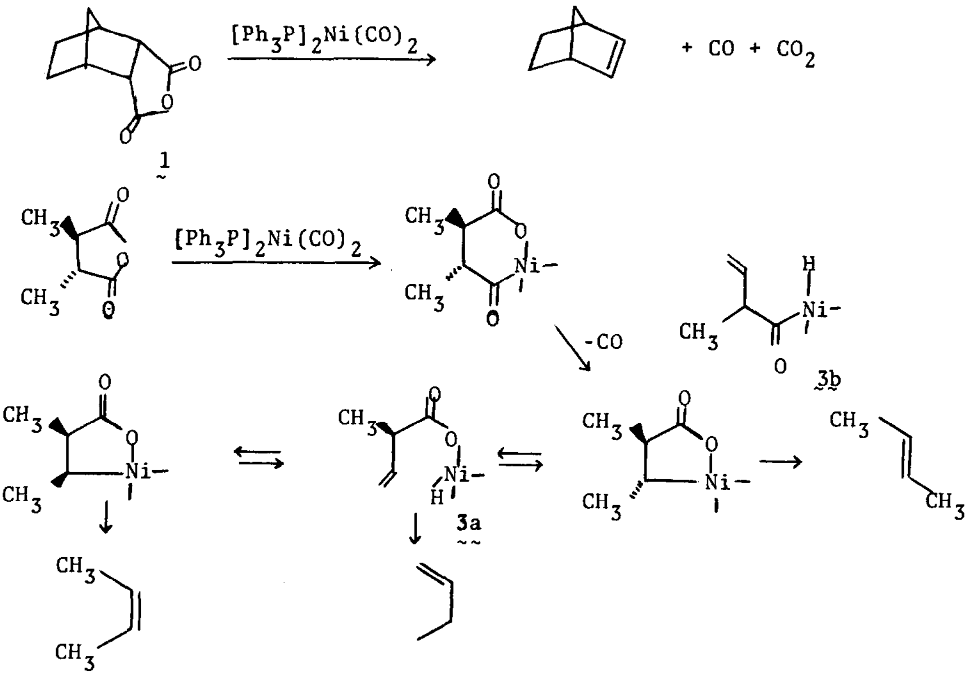
The ability to convert bis-carboxylic acids to olefins constitutes a valuable synthetic transformation. Techniques to accomplish this reaction focus around traditional oxidative decarboxylations. The lead tetraacetate method has had variable success;[2] it sometimes has been superseded by carbonium ion rearrangements.[3] Electrolytic techniques appear to circumvent some of these problems;[4] however, it appears limited to small scales and is rather inconvenient. The decomposition of bis peresters has not been studied sufficiently to comment on its general utility.[5] We wish to report a new method for such eliminations, which involve a novel use of various transition metals to effect elimination.[6]

Treatment of endo-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid anhydride (1) with bis-triphenylphosphinenickel dicarbonyl[7] in triglyme (initially at 80° and slowly raising it to 200° during which time the product is being swept continuously from the reaction mixture) generates a 53% yield of bicyclo[2.2.1]heptene. Whereas, the reaction of 1 proceeded cleanly to produce the desired olefin as the only hydrocarbon product, the reaction of anhydrides possessing abstractable β hydrogens, e.g. 2,3-dimethylsuccinic anhydride 2, produces more complex reaction mixtures.

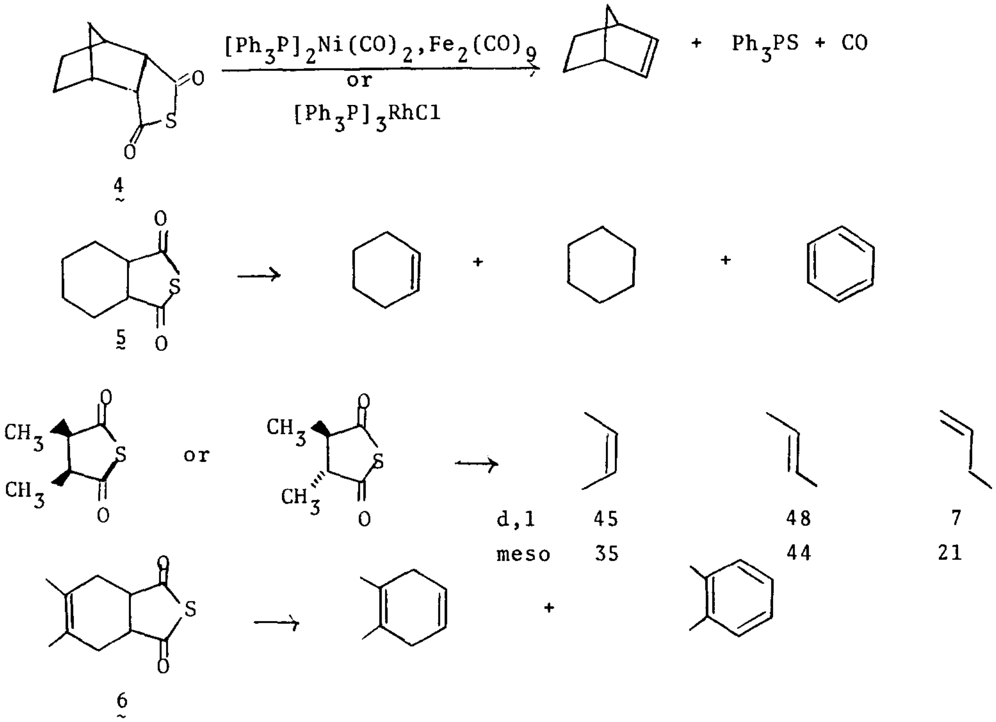
Treatment of anhydride 2 under identical conditions generates, in addition to trans-2-butene, both cis-2-butene and 1-butene in the approximate ratio of 1:1:0.1. Suitable control experiments demonstrated no interconversion of olefins under the reaction conditions. A rationale for these products appears in Scheme I.[8] Formation of a species such as 3 explains the loss of stereochemistry and double bond migration observed.

Scheme I. Nickel Catalyzed Eliminations of Anhydrides.



In an attempt to extend and improve the procedure, elimination of thioanhydrides was examined. These substances are available by treatment of the anhydrides with sodium sulfide.[9] Elimination proceeded with bis-triphenylphosphinenickel dicarbonyl, diiron nonacarbonyl, and tris-triphenylphosphinerhodium chloride[10] (see Scheme II). In general, the yields of olefin are higher than from the corresponding anhydride although

Scheme II. Eliminations of Thioanhydrides.



the reaction does not appear to be practical for thioanhydrides possessing abstractable β-hydrogen. Thus, the thioanhydride 4 produces norbornene in yields up to 56%; however, the thioanhydride of cis-cyclohexane-1,2-dicarboxylic acid 5 yielded disproportionation products (cyclohexane and benzene) in addition to the desired olefin; the latter formed in 28% yield utilizing the nickel complex. Aromatization becomes the major process for thioanhydride 6 in which a 33% yield of o-xylene and only a 1% yield of 2,3-dimethyl-1,4-cyclohexadiene was obtained.

These results are compatible with rationale similar to that proposed for the anhydride elimination. Further support arises from consideration of the decomposition of meso- or d,l-2,3-dimethylsuccinic thioanhydride. In both cases, cis- and trans-2-butene and 1-butene are obtained (total yield of olefins is 16%) in the relative amounts shown in Scheme II. Control experiments again show no olefin interconversion. In the thioanhydride elimination, triphenylphosphine thiooxide can be isolated. Thus, it appears that carbon monoxide and the thiooxide are produced instead of carbonyl sulfide as might have been expected by analogy to the carbon dioxide produced in the anhydride elimination. Utilization of complexes of manganese or palladium was unfruitful.

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