

THERMAL DECOMPOSITION OF 1,2-BIS(HYDROXYDIPHENYLMETHYL) COMPOUNDS ¹⁾

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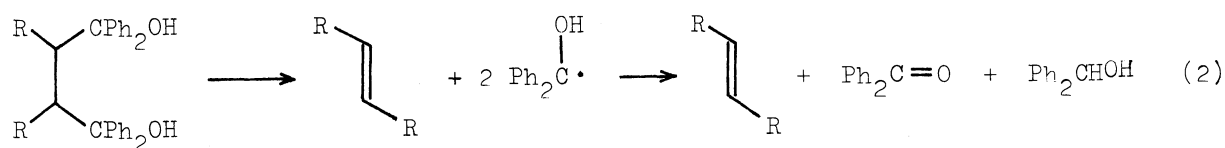
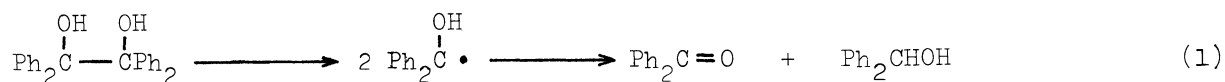
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Thermal decomposition of 1,2-bis(hydroxydiphenylmethyl) compounds was investigated for the formation of olefins. Several examples showed that the reaction was useful for olefin synthesis; however, in some cases retro Diels-Alder and dehydration reactions took place. The reaction mechanisms for the formation of the olefins and other products were discussed.

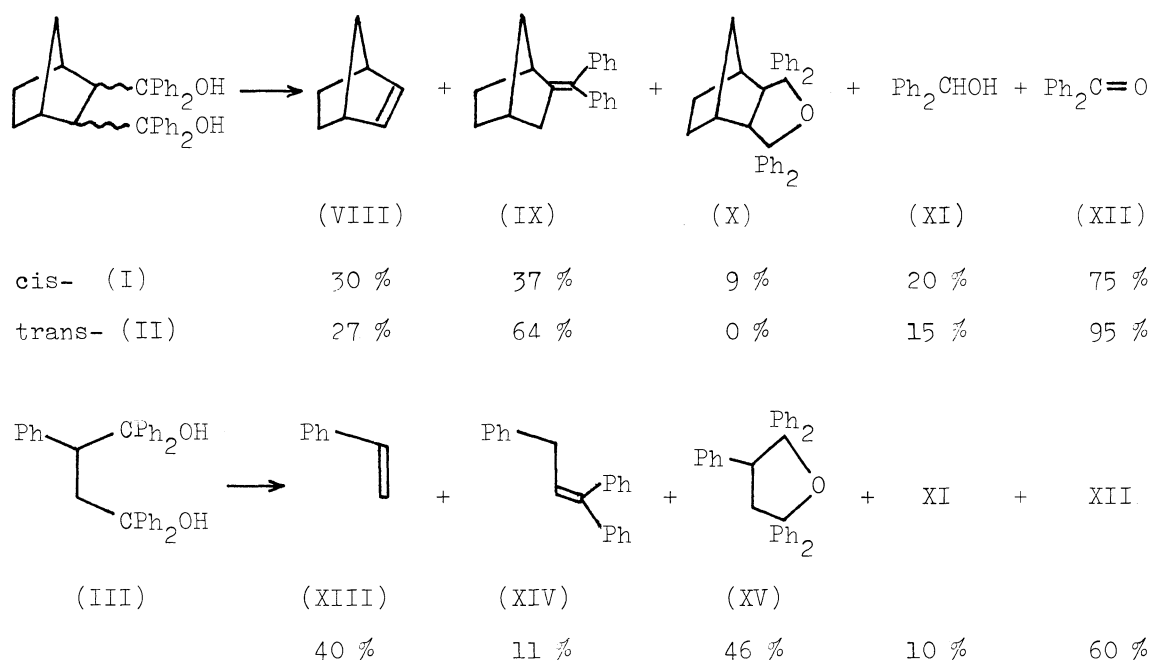
Several methods for the conversion of 1,2-dicarboxylic acids to olefins; oxidative decarboxylation with lead tetraacetate,^{2,3)} electrolysis,^{4,5)} decomposition of bisperesters,⁶⁾ and pyrolysis with transition metal complexes⁷⁾ are known. However, these methods are not necessarily satisfactory, because of undesired rearrangements, rather poor yields, limitation to a small scale experiment, and a lack of a general utility.

Recently, Neckers and Colenbrander have reported a thermal decomposition of benzpinacol affording benzophenone and benzhydrol,⁸⁾ and proposed equation (1) for the mechanism. It is expected that upon heating of 1,2-bis(hydroxydiphenylmethyl) compounds (1,4-glycols) an analogous decomposition may take place to form olefins as shown in equation (2).



With such an expectation, we have investigated the thermal decomposition of the following 1,4-glycols; cis- (I)⁹⁾ and trans-2,3-bis(hydroxydiphenylmethyl)-bicyclo[2.2.1]heptane (II),⁹⁾ 1,1,2,4,4-pentaphenylbutane-1,4-diol (III),¹⁰⁾ cis-endo-6,7-bis(hydroxydiphenylmethyl)tricyclo[3.2.2.0^{2,4}]nona-8-ene (IV), cis-endo-2,3-bis(hydroxydiphenylmethyl)bicyclo[2.2.1]hept-5-ene (V), o-bis(hydroxydiphenylmethyl)benzene (VI),¹¹⁾ and trans-1,2-bis(hydroxydiphenylmethyl)spiro[2,6]nona-4,6,8-triene (VII).¹²⁾ They were readily synthesized by the reaction of the corresponding 1,2-bis(methoxycarbonyl) compounds with phenyllithium.

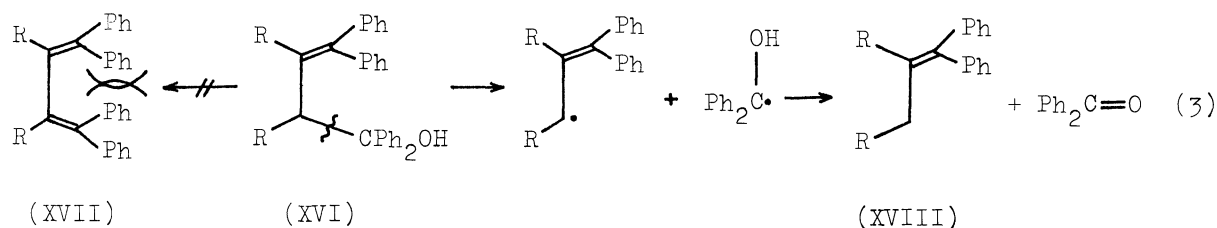
Glycols I, II and III on heating at a temperature between 250 to 290°C produced the desired olefins (VIII and XIII). During thermolysis, however, undesirable products such as diphenylethylene derivatives (IX and XIV) and dehydration products were formed. The unexpected yields of benzophenone and benzhydrol can reasonably be explained by the conversion of benzhydrol into benzophenone in almost 30% yield under the same conditions.



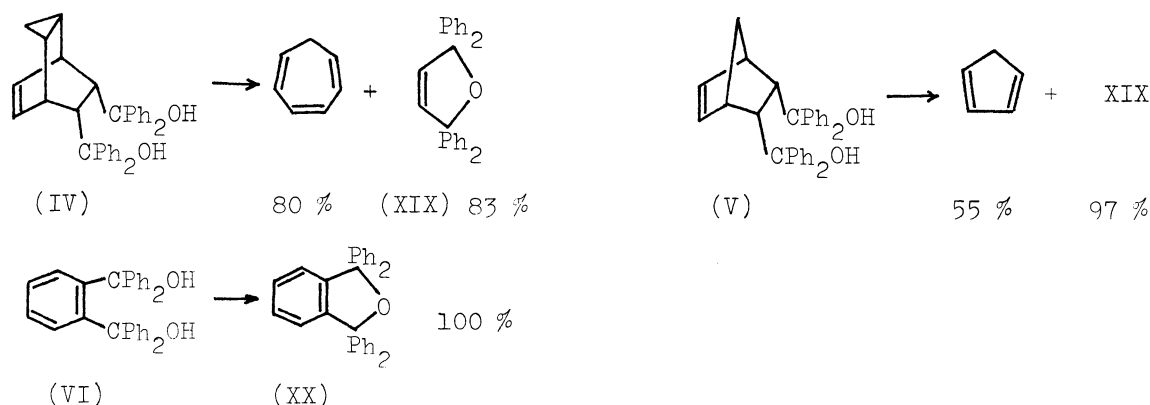
Scheme I

If the olefins are formed according to equation (2), there would be no difference for the formation of olefin (VIII) from cis- (I) and trans-1,4-glycols (II). In fact, I and II afforded norbornene (VIII) in almost the same yields. The formation of diphenylethylene derivatives (IX and XIV) is explained as follows; the homolytic bond cleavage was preceded by dehydration to give XVI which in turn underwent

the homolytic bond cleavage at the allylic position and afforded benzophenone and diphenylethylene derivative (XVIII)¹³⁾ as shown in equation (3). Some other mechanisms are also possible.¹⁴⁾ The reason why butadiene derivative (XVII) was not formed is ascribed to the steric repulsion between phenyl groups.

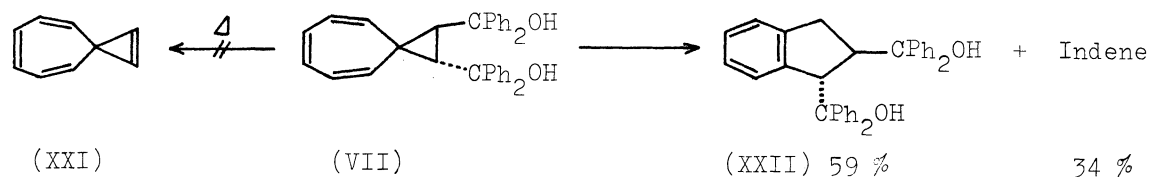


As shown in Scheme II, in some cases, retro Diels-Alder reaction and/or dehydration took place as major reaction. For instance, when VI was attempted to pyrolyze, only the dehydration took place to give 2,2,5,5-tetraphenyl-3,4-benzodihydrofuran (XX).



Scheme II

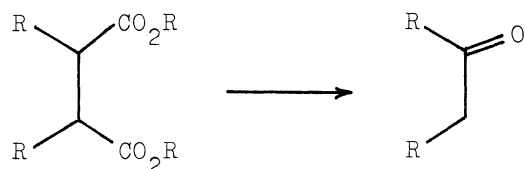
In order to synthesize spiro[2,6]nona-1,4,6,8-tetraene (XXI), VII was pyrolyzed under the conditions described above. However, XXI was not obtained and instead indene and trans-1,2-bis(hydroxydiphenylmethyl)indane (XXII) were isolated. The structure of XXII was confirmed by the synthesis from dimethyl indane-trans-1,2-dicarboxylate.¹⁵⁾ Thermolysis of XXII afforded indene together with benzophenone and benzhydrol. These results suggest that XXII was firstly formed from VII by the 1,7-carbon migration¹⁵⁾ and in turn converted thermally into indene.



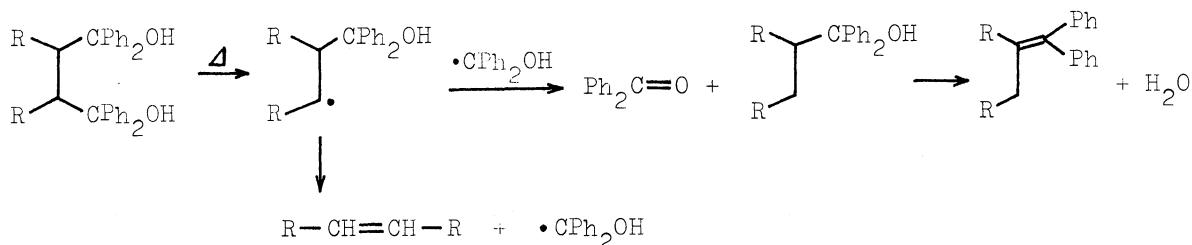
Scheme III

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- 13) The formation of diphenylethylene derivatives suggests a synthetic route to carbonyl compounds from 1,2-dicarboxylic acids.



- 14) A referee suggested possibility of a stepwise decomposition way. We are indebted to the referee.



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