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NOVEL RING-ENLARGEMENT REACTION OF DIPHENYLCYCLOPROPENONE WITH 2,6-DIMETHYLPHENYLISONITRILE IN THE PRESENCE OF TRIPHENYLPHOSPHINE

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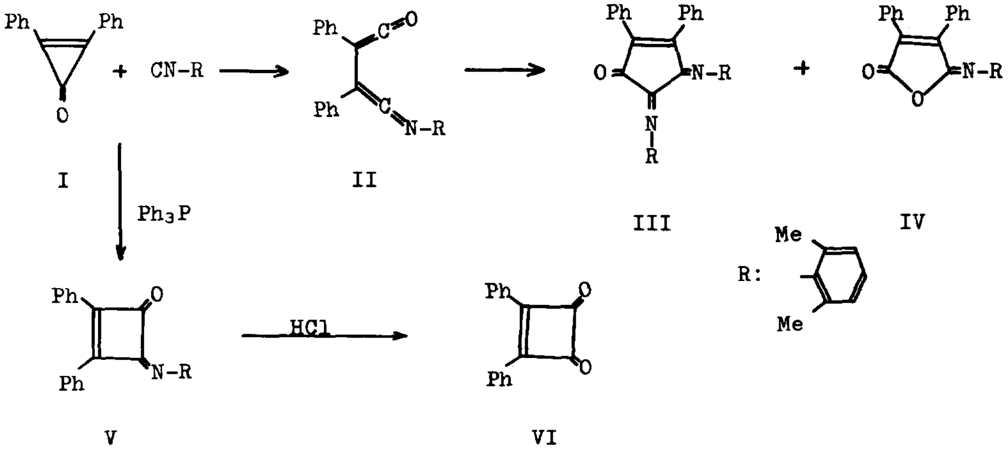
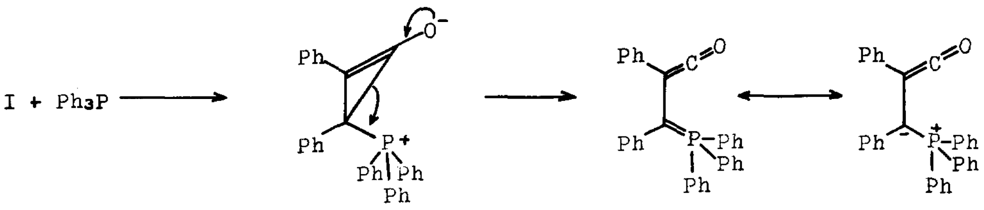
In an earlier communication(1) we reported the reaction of diphenylcyclopropenone (I) with 2,6-dimethylphenylisonitrile to give the ring expanded products (III) and (IV), presumably via a primary ring-opening intermediate,i.e., monoimine of bisketene (II) as the result of a Michael addition of isonitrile. Such a Michael addition of isonitrile to cyclopropenone had not been reported(2). We have now found the quite different type of ring-enlargement reaction of diphenylcyclopropenone in the presence of triphenylphosphine which has the ability of a Michael addition(3).



When the reaction of I with a molar equivalent of 2,6-dimethylphenylisonitrile was carried out in the presence of catalytic amount of Ph_3P in benzene for 24 hours at room temperature under nitrogen atmosphere, the sole reaction product, 4-(2,6-dimethylphenylimino)-2,3-diphenylcyclobuten-1-one (V) (mp 101-102°) was obtained in 84 % yield and Ph_3P used was quantitatively recovered. The structure of V was established by the elemental analysis, the molecular weight determination and the following spectral observations: characteristic IR absorptions at 1768 cm^{-1} ($\nu_{C=O}$) and 1697 cm^{-1} ($\nu_{C=N}$): UV maxima in ethanol at 270 mμ (log ε 4.34), 290 mμ (log ε 4.32) and 328 mμ (log ε 4.21): NMR signals at 1.65τ (m,2H), 2.15τ (m,2H), 2.55τ (m,6H), 3.13τ (m,3H) and 7.88τ (s,6H). The structure of V was confirmed further by its hydrolysis. Iminocyclobutenone V was easily hydrolyzed by dilute hydrochloric acid to give diphenylcyclobutenedione (VI)(4) which was identified by the comparison of infrared spectrum and mixture melting point with that of authentic sample(5).

To investigate such a catalytic action of Ph_3P, the equimolar mixture of I and Ph_3P was stirred under a similar condition as above to produce the reddish yellow solution. The reaction could be conveniently monitored by an infrared spectroscopy. The infrared spectrum of this solution showed the characteristic strong peak at 2080 cm^{-1} which was presumably due to the carbonyl streching of the ketene(6). The ultraviolet spectrum of this solution showed a shoulder at 350 mμ, which might be that expected from a conjugated phosphorane chromophore(7). When O_2 was bubbled into this solution, besides unidentified compounds triphenylphosphinoxide was obtained in 41 % yield(8). The cleavage of P-C bond in phosphorane by O_2 to give phosphinoxide is well established reaction(7,9). All these observations suggest the formation of ketene-phosphorane (VII)(10) which was produced by an initial Michael addition of Ph_3P to the activated double bond of I followed by ring cleavage.

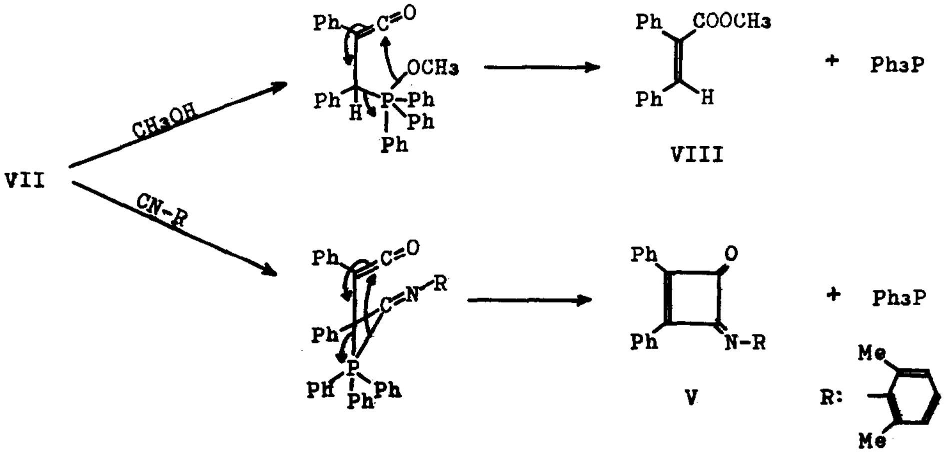


VII

Then the reaction of VII in benzene with 2,6-dimethylphenylisonitrile at room temperature under nitrogen atmosphere also resulted in the formation of V in good yield and Ph_3P was recovered almost quantitatively. Consequently, VII should be actually the intermediate in the reaction of diphenylcyclopropenone with isonitrile in the presence of Ph_3P.

Now, the treatment of VII in benzene with methanol gave methyl cis-2,3-diphenylacrylate (VIII) in 71 % yield and Ph_3P was recovered almost quantitatively. On the other hand, when ketene-phosphorane formed by the reaction of I with triethylphosphite was treated with methanol, both methyl (VIII) and ethyl cis-2,3-diphenylacrylate (IX) was obtained in a moderate yield. No trans isomer was isolated in both reactions as above. The structure of VIII and IX were determined by comparison with authentic specimens(11). Its cis structure was confirmed further by the UV spectrum which was very similar to that of cis-stilbene(12). It seems that these facts indicate the formation of cis acrylate VIII is the result of addition of methanol to double bond of phosphorane VII and intramolecular esterification of ketene(e.g., P-O bond rearrangement) followed by the elimination of Ph_3P.

Thus the formation of iminocyclobutenone V from VII might be taking a route of the addition of isonitrile to double bond of phosphorane VII and the concerted rearrangement of P-C bond followed by the elimination of Ph_3P as shown in the following scheme, although other mechanism (e.g., ionic or radical) cannot be excluded completely on the basis of present evidence.



It seems that these reactions via ketene-phosphorane might be of considerable utility, and further studies to explore its possibility and mechanistic investigation are in progress.

References

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