for help and discussions. S.A. is obliged to Professor M. Eigen for encouragement.

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(19) This work is based on the Ph.D. dissertation of S.A.

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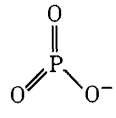
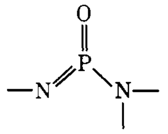
The Three-Phase Test for Reaction Intermediates. Metaphosphates

Sir:

Monomeric metaphosphates have been implicated as intermediates in a variety of phosphorus transfer reactions.[1,2] The hydrolysis of monoalkyl,[3] aryl,[4] and acyl[5] phosphates and the decomposition of β-halophosphonates[6] can all be interpreted as proceeding via the elusive parent ion, I. Kinetic evidence has similarly indicated II, a metaphosphorimidic amide, during the hydrolysis of phosphorodiamidic halides and pyrophosphates,[7] whereas stereochemical evidence has been used to support the intermediacy of III, a metaphosphoniminate.[8] Most recently, trapping[9] and spectroscopic[10] evidence for metaphosphate intermediates have been presented and prompt this report of new evidence for the intermediacy of II, using an experimental technique which differs *in kind* from previous methods.



I



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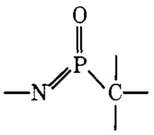
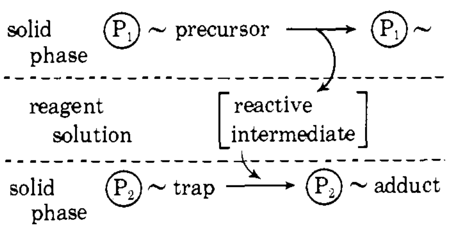


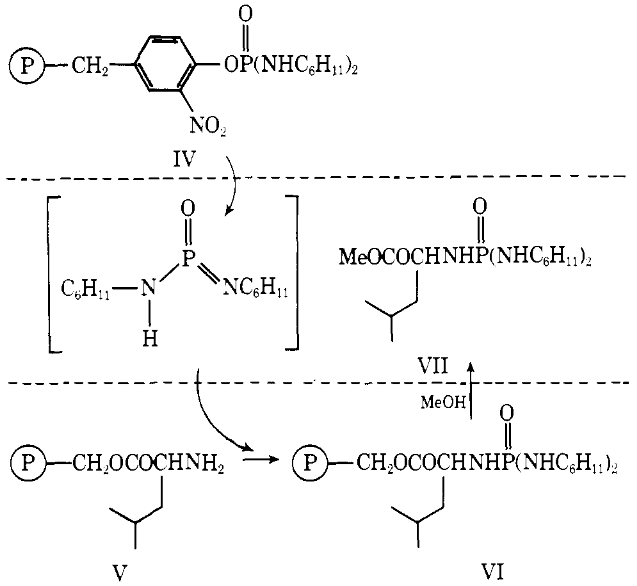
III

In a recent communication[11] we described an unambiguous test for reaction intermediates (Scheme I). The technique involves the generation of a reaction intermediate from an insoluble, polymer-bound precursor and its trapping on a second solid phase suspended in the same solution. Since the direct reaction of the two polymers is physically precluded, the formation of an adduct during the three-phase experiment requires the existence of a polymer-free intermediate. Application of the three-phase test for the detection of an intermediate in phosphorodiamidate transfer was accomplished as follows.

Scheme I

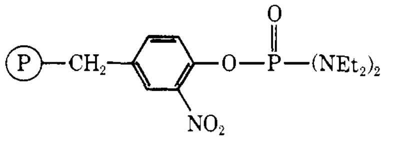


Scheme II



Macroreticular, cross-linked polystyrene (Rohm & Haas XE 305) was alkylated with 3-nitro-4-hydroxy benzyl chloride according to Patchornik's procedure,[12] and the resulting polymer-bound nitrophenol was phosphorylated with *N*,*N*-dicyclohexylphosphorodiamidic chloride to yield the precursor resin IV (Scheme II). The trapping agent V was prepared from chloromethylated polystyrene Merrifield's resin, Cal Biochem) by esterification to *tert*-butoxycarbonyl-L-leucine followed by N deblocking according to standard procedures.[13] When a suspension of IV and V in dioxane was treated with 1,8-bis(dimethylamino)naphthalene (proton sponge), phosphorodiamidate transfer could be detected on the resin VI (ir 1240 cm^{-1}). The adduct was removed from VI by dimethylaminoethanol-catalyzed transesterification to give VII, identical with an authentic sample.[14] Therefore, a phosphorylating agent must have been present in solution during the three-phase experiment.

While the existence of an intermediate is readily established, the structure of the phosphorylating agent cannot be specified with certainty. The isolation of a monophosphorylated product is consistent with the intermediacy of a monomeric metaphosphate, but dimers or oligomers of the metaphosphate cannot yet be excluded as the actual phosphorylating agent(s). It is unlikely that the phosphorylating agent is a phosphorylated proton sponge (i.e., nucleophilic catalysis of phosphate transfer) since this base has an extraordinary low nucleophilicity toward electrophiles other than protons.[15] Further, in full agreement with the predictions of Westheimer,[7c] no evidence for phosphate transfer could be found when the fully substituted VIII was used in place of IV during the three-phase test; thus an elimination–addition mechanism involving the metaphosphate (meta-



VIII

phosphorimidic amide) is indicated. Application of this method to the parent monomeric metaphosphate ion is in progress.

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(14) This compound was characterized by the expected spectroscopic features and gave satisfactory elemental analyses.
(15) It is possible that the actual phosphorylating agent is complexed with dioxane; at present we are unable to distinguish between such a complex and solvated metaphosphate.
(16) Visiting Fulbright Scholar on leave from the University of Valencia, Valencia, Spain.

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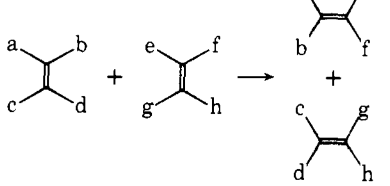
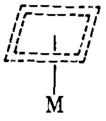
The Mechanism of the Olefin Metathesis Reaction

Sir:

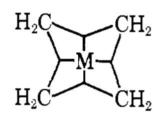
The olefin metathesis reaction generalized as in eq 1 is effected by catalysts usually containing tungsten, molybdenum, or rhenium.[1] On the basis of the gross structural change, mechanism I was suggested,[2,3] but to account for the three facts, (1) that no cyclobutane has been found to evolve from the reaction, (2) that no cyclobutane has been found to enter into the reaction,[4a,5] and (3) that cyclobutane has no accessible valencies for bonding to metals, seemed to require either unusual theories for the bonding in I[6] or the proposition that the key intermediate be instead the multicentered species II.[4a,7] An alternative mechanism postulates the transformation shown in eq 2,[8] but this would also be unusual.



(1)



I



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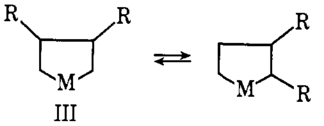
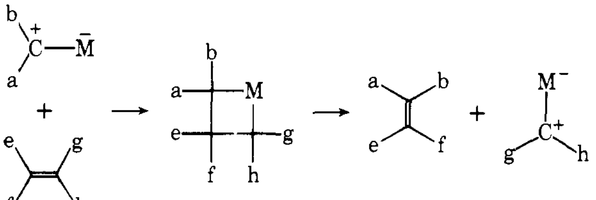


III

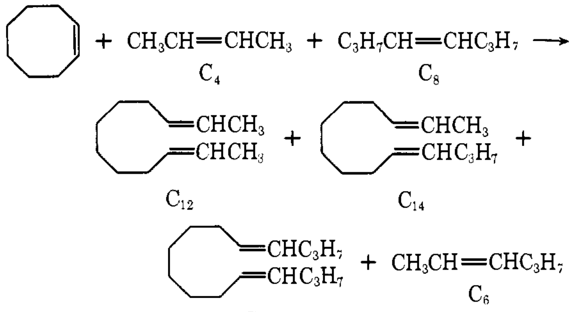
(2)

Probably none of these schemes is correct and the actual mechanism is the chain reaction 3. Since metal-carbenes[9] and four-membered rings containing metals[10] are known species and additions to olefins are common, this proposal requires no unusual theoretical explanation, and we show below that it accounts for all the known facts about olefin metathesis. The importance of this theory is that it can be applied widely to make predictions. The major difficulty is finding a way to prove it.[11]



(3)

Consider the following experimental test, the reaction of a cyclic olefin like cyclooctene with a mixture of 2-butene and 4-octene. According to any of the schemes the C_{12}, C_{14}, and C_{16} dienes (eq 4) should form ultimately, but according to the schemes in which I, II, and III form in the rate-determining step, the ratio of C_{14} and C_{12} or of C_{14} and C_{16} would have to be zero initially. In contrast, Scheme I indi-



Scheme I