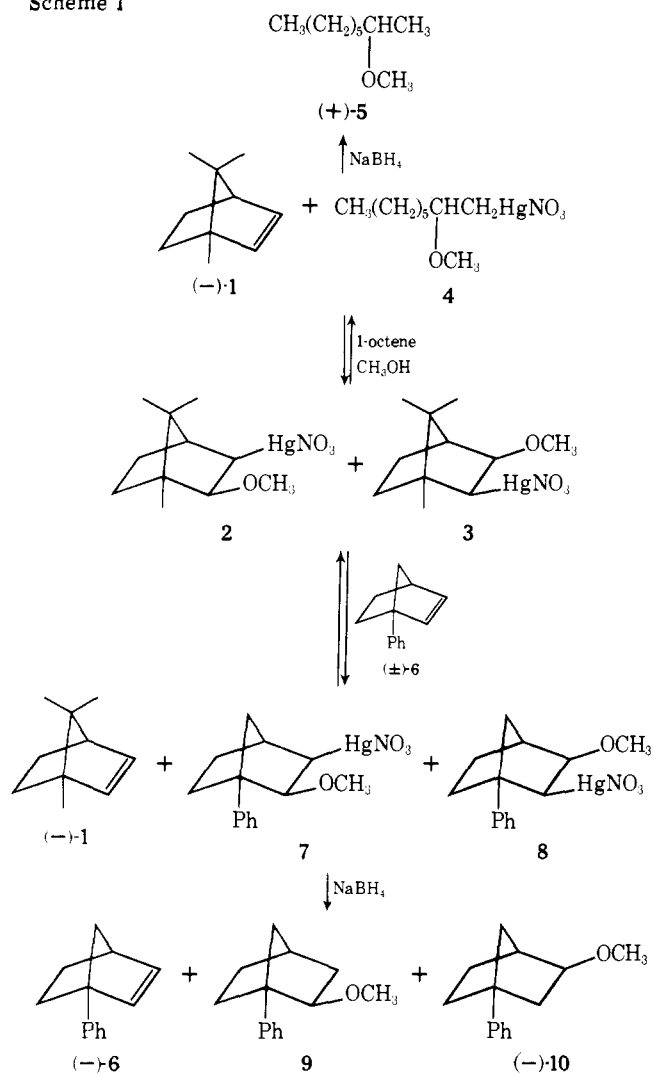
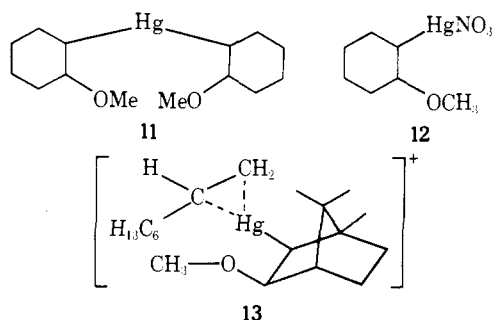


Scheme I



netic data.¹ More significantly, however, our results provide compelling evidence that the optically active oxymercurial and the exchanging alkene are in very close proximity in the transition state. The steric bulk of the exchanging alkene is also of obvious importance since exchange reactions of **2** and **3** with norbornene and *trans*-cyclooctene did not result in significant asymmetric induction.

The above results, however, do not necessarily exclude a transient dialkoxymercurial intermediate (eq 4). Consequently, we synthesized¹⁰ the dialkoxymercurial **11** and examined its reactivity under typical exchange conditions. Treatment of **11** with 1 equiv of $\text{Hg}(\text{NO}_3)_2$ in CH_3OH afforded the methoxymercurial **12**¹¹ as determined by nmr analysis ($\delta(\text{OCH}_3)$ 3.345 ppm, analyzed as the mercurichloride). However, treatment of **11** with 1 equiv of **12** in CH_3OH resulted in >90% decomposition of **11** (135 min)



with formation of **12**, elemental mercury, cyclohexene, and an unidentified methoxymercurial. Compound **11** is stable in neutral CH_3OH ,¹¹ but it does not exchange with 1-octene.¹¹ More significantly, **11** is *not* stable in the presence of protic acid in methanolic solution. One equivalent of nitric acid in CH_3OH solution effected complete cleavage¹¹ of the carbon-mercury bond in **11** affording **12** and cyclohexyl methyl ether. However, a stirring solution of **12** in the presence of 1 equiv of cyclohexene and HNO_3 (*i.e.*, degenerate exchange conditions) failed to produce a detectable amount of cyclohexyl methyl ether or other side products even after 5 days. These results are, therefore, not consistent with eq 4 where acid cleavage (k_4) would afford an alkene and an alkoxymercurial.

The above observations support our earlier suggestion that alkene exchange proceeded by electrophilic addition of the mercury of the oxymercurial to the exchanging alkene affording a bisalkene mercury cation such as **13**. A more precise assignment of the mechanism must await detailed kinetic studies of this alkoxy-exchange reaction. The involvement of **13** is consistent with the rate law given in eq 2¹ for exchange of hydroxymercurials where $k_3' \gg k_2$ and is supported by the unusually high optical yields obtained in the present work.

Acknowledgment. Acknowledgment is made to the National Institutes of Health (ES 00761-03) for support of this work.

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- The use of equimolar amounts of HgX_2 and HgO affords the oxymercurial in the absence of the mole of HX usually produced.
- The per cent exchange was kept at a minimum since the degenerate exchange of **4** with 1-octene resulted in a loss of optical activity.
- Optically pure (*S*)-(+)-2-methoxyoctane (**5**) having $[\alpha]_D +10.7^\circ$ was prepared from 2-octanol $[\alpha] +11.2^\circ$, CCl_4 (92% optically pure)⁷ by the action of NaH and CH_3I in ether.
- E. G. Av, R. C. Sigler, G. Fischer, and D. Nurok, *J. Gas Chromatogr.*, **4**, 51 (1966).
- The structure of **9** was established by an independent synthesis from 2-hydroxy-1-phenylnorbornane. The *exo* stereochemistry of **7**, **8**, **2**, and **3** was based upon nmr analysis.⁹ The structure of **2** was also established by independent synthesis of the corresponding methyl ether from isborneol.
- R. F. Richter, J. C. Philips, and R. D. Bach, *Tetrahedron Lett.*, 4327 (1972).
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- A reaction time of 25 min was used since exchange of **12** ($\text{X} = \text{ClO}_4$) with 1-octene in CH_3OH was at least 80% complete in that time in the presence of 1 equiv of acid.

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The Three-Phase Test for Reaction Intermediates. Nucleophilic Catalysis and Elimination Reactions

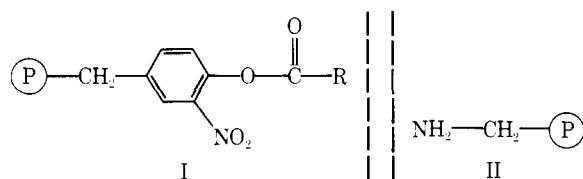
Sir:

In a recent communication¹ we introduced a technique for the detection of reaction intermediates which promises to be of complementary value to direct observation and kinetic methods. The technique involves the generation of a reaction intermediate from an insoluble polymeric precursor, and its detection by trapping on a second solid phase suspended in the same solvent (Scheme I).

Unlike classical trapping experiments, the direct reaction of precursor and trapping agent is physically prohibited in

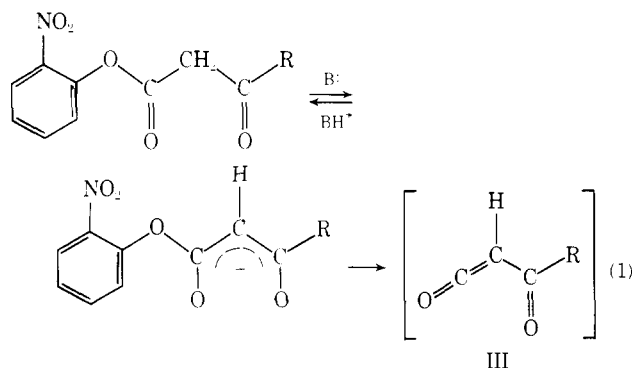
this three-phase test. Therefore, observed reactions between the two polymers provide *prima facie* evidence for the existence of free reaction intermediates.

The new method is especially suited to the detection of nucleophilic catalysis. Acyl imidazoles have been spectrophotometrically observed² during the imidazole-catalyzed hydrolysis of *o*-nitrophenyl esters, but nucleophilic catalysis is most frequently detected by kinetic or a combination of kinetic and trapping methods.³ For the three-phase test, the polymer-bound esters, I, readily available through Patchornik's procedure,⁴ and the polymeric benzyl amine, prepared from Merrifield resin *via* Gabriel synthesis,⁵ provided the necessary precursors and trapping agent, respectively.

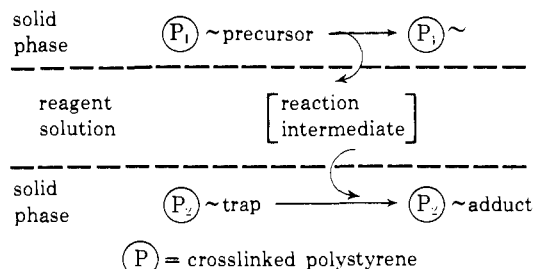


A mixture of I ($R = \text{CH}_3$; ν 1770 cm^{-1}) and II suspended in CHCl_3 at 50° remained unchanged even when the beads were ground together with solvent in a mortar. However, the addition of a catalytic (10%) amount of imidazole resulted in the acylation of II (ν 1680 cm^{-1}) and a corresponding disappearance of the active ester of I ($t_{1/2} \sim 4$ hr at 50°). Similar behavior was observed with the benzyloxy-carbonyl glycine derivative ($R = \text{CH}_2\text{NHZ}$) in aqueous dioxane at 50° . Nucleophilic catalysis of the transfer of this group between the two resins was detected⁶ with (in decreasing order of efficiency) imidazole, *N*-hydroxybenzotriazole, *N*-hydroxyphthalimide, and *N*-hydroxysuccinimide. While traces of acyl transfer could be observed with pyridine (in the presence of fluoborate), acetone oxime, the tetramethylammonium salt of benzyloxycarbonyl glycine, and 1,2,4-triazole, the major reaction observed with these catalysts was slow hydrolysis of the polymeric active ester.

Intermediates in elimination reactions could also be detected through the three-phase test. Thus I ($R = \text{NHC}_6\text{H}_5$) rapidly carbamylated the amine II ($t_{1/2} = 5$ min) when a suspension of both was treated with triethyl amine or proton sponge (1,8-bis(dimethylamino)naphthalene) in dioxane. The intermediate phenylisocyanate (believed to be on the hydrolytic pathway of these esters in solution⁷) could readily be observed by *ir* in the solution between the two resins. Similarly, acyl transfer to II was observed when the precursors I, $R = \text{CH}_2\text{CO}_2\text{Et}$ and $R = \text{CH}_2\text{COCH}_3$, were treated with triethylamine in dioxane. Although the acylating agents cannot be identified with certainty, these cases closely parallel Bruice's E_{1cB} reactions,⁸ for which ketenes have been postulated and III ($R = \text{CH}_3$) has been trapped⁹ (eq 1).



Scheme I



Experiments designed to test the scope of the three-phase test and its applicability to intermediates in phosphate transfers are underway.

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Synthesis of Icosahedral Nickelaboranes

Sir:

We wish to report the synthesis of the first icosahedral metalloborane species derived from the hypothetical $B_{11}H_{11}^{4-}$ and $B_{10}H_{10}^{6-}$ ions. The compounds, $(C_5H_5)_2Ni(B_{11}H_{11})$ (I) and $[(C_5H_5)_2Ni]_2B_{10}H_{10}$ (II) are the first representatives of a potentially vast and as yet unexplored area of polyhedral metalloborane chemistry, and these are in fact the first examples of polyhedral metalloboranes without "extra hydrogens."¹

To a solution of 2.0 g (11 mmol) of $Na_2B_{11}H_{13}$ in 200 ml of acetonitrile, 10 g of 0.48% Na-Hg (2.1 mmol of reductant) was added, followed by 2.1 g (11 mmol) of $Ni(C_5H_5)_2$. The mixture was stirred overnight under N_2 , the solvent was removed, and 150 ml of H_2O was added. The solution was filtered through Celite and excess $(CH_3)_4NCl$ was added. The dark greenish yellow solid was isolated by filtration and recrystallized from acetone- H_2O to give 2.4 g (63%) of bright yellow $(CH_3)_4NB_{11}H_{11}NiC_5H_5$. Alternatively the closo borane anion, $B_{11}H_{11}^{2-}$, as the tetrabutylammonium salt, reacted with $[C_5H_5NiCO]_2$ in tetrahydrofuran at reflux to give the deep yellow complex, I, in 23% yield. *Anal.* Calcd for $B_{11}C_9H_{28}NNi$: B, 36.26, C, 32.96; H, 8.61; N, 4.27; Ni, 17.90. Found: B, 35.90 C, 33.15; H, 8.58; N, 4.27; Ni, 17.52. The electronic spectrum through 8000 Å was dominated by a single strong absorption in dichloromethane 271 (52,000) (λ_{max} , $m\mu(\Sigma_{max})$).