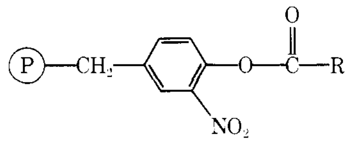
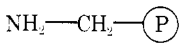
this three-phase test. Therefore, observed reactions between the two polymers provide *prima facie* evidence for the existence of free reaction intermediates.

The new method is especially suited to the detection of nucleophilic catalysis. Acyl imidazoles have been spectrophotometrically observed[2] 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.



I

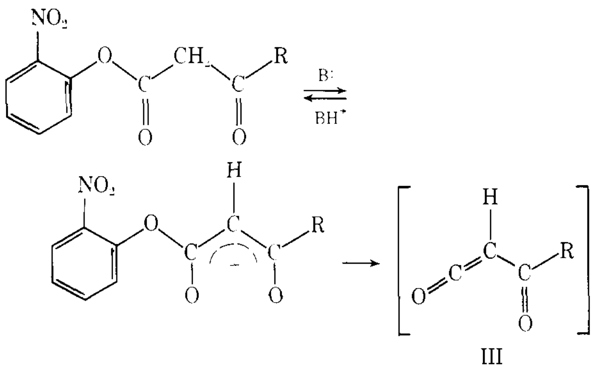


II

R = CH_3, CH_2NHZ, NHC_6H_5, CH_2COCH_3, CH_2CO_2Et

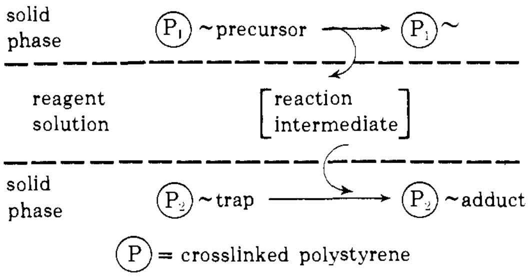
A mixture of I (R = CH_3; ir 1770 cm^{-1}) and II suspended in $CHCl_3$ at 50° remained unchanged even when the beads were ground together with solvent in a mortar. However, the addition of a catalytic (10%) amount of imidazole resulted in the acylation of II (ir 1680 cm^{-1}) and a corresponding disappearance of the active ester of I ($t_{1/2}$ ~4 hr at 50°). Similar behavior was observed with the benzyloxycarbonyl glycine derivative (R = CH_2NHZ) in aqueous dioxane at 50°. Nucleophilic catalysis of the transfer of this group between the two resins was detected[6] 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 = NHC_6H_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 solution[7]) 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 = CH_2CO_2Et and R = CH_2COCH_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 = CH_3) has been trapped[9] (eq 1).



III (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, $(C_5H_5)Ni(B_{11}H_{11})$ (I) and $[(C_5H_5)Ni]_2B_{10}H_{10}$ (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}, mμ(Σ_{max})).

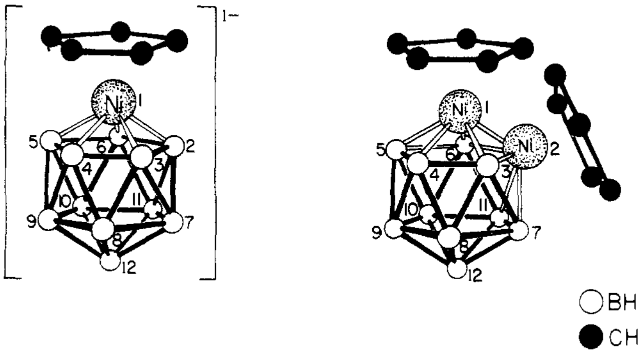

Figure 1. Proposed structures of $[(B_{11}H_{11})Ni(C_5H_5)]^-$ and $B_{10}H_{10}(NiC_5H_5)_2$.

Good yields of I were also obtained by treating $[(C_4H_9)_4N]B_{11}H_{13}$ with $(C_5H_5)_2Ni$ in refluxing 1,2-dimethoxyethane in the absence of a reductant; however, the reaction proceeded only very slowly at room temperature. With the addition of catalytic amounts of Na–Hg, the reaction went to completion in several hours. The noncondensable gas evolved in the reaction was collected and identified as H_2. Slightly more than 1 mol of H_2 was produced for each mole of I isolated on work-up.

The 80.5-MHz ^{11}B nmr spectrum of I in acetonitrile consisted of three sharp doublets of relative area 1:5:5 at −19.9(134), −16.0(135), and +5.1(128) (chemical shift, ppm, relative to $BF_3{\cdot}O(C_2H_5)_2$ (coupling constant, Hz)). The 60-MHz proton nmr spectrum was obtained in acetonitrile solution and consisted of two sharp singlets with relative area 5:12 at τ 4.62 and 6.95, respectively. The former resonance was assigned to the cyclopentadienyl moiety and the latter to the methyl protons of the tetramethylammonium cation. Distinctive infrared absorptions appeared at 2490 (s), 1020 (s), 950 (s), 910 (m), 829 (m), 728 (m) (cm^{-1} (intensity); taken in a Nujol mull). Cyclic voltammetry in acetonitrile demonstrated a reversible reduction wave at $E_{p/2} = -1.50$ V. These data are consistent with the icosahedral structure represented in Figure 1.

The reaction of $[(CH_3CH_2)_3NH]_2B_{10}H_{10}$ in 1:3 acetonitrile:1,2-dimethoxyethane with an equimolar amount of $[CpNiCO]_2$ afforded a deep brown solution. Column chromatography on Florisil with dichloromethane–hexane as eluant afforded golden brown crystals of II in 45% yield. An alternative method of preparation of II which gave high yields (70%) involved the direct interaction of quaternary ammonium salts of $B_{10}H_{10}^{2-}$ with $(C_5H_5)_3Ni_2^{+}$[2] in tetrahydrofuran. *Anal.* Calcd for $B_5C_5H_{10}Ni$: B, 29.55; C, 32.83; H, 5.52; Ni, 32.10. Found: B, 29.88: C, 32.62; H, 5.44; Ni, 31.48. Mass spectral data proved the peak of maximum intensity in the parent envelope to be at *m/e* 363. A peak of medium intensity occurred at *m/e* 188 and a smaller peak occurred at *m/e* 190 which were assigned to the $(C_5H_5)_2\,{}^{58}Ni^+$ and $(C_5H_5)_2\,{}^{60}Ni^+$ ions, respectively. The electronic spectrum in dichloromethane was 475 (755), 376 (3880), 300 (23,900), 239 (64,400) ($\lambda_{max}m\mu(\Sigma_{max})$).

The ^{11}B nmr spectrum of II at 80.5-MHz consisted of four doublets with relative area 1:1:2:1 at −54.3 (138), −26.1 (134), −21.3 (150), and −6.7 (144 (chemical shift, ppm, relative to $BF_3{\cdot}O(CH_2CH_3)_2$ (coupling constant, Hz)). The 60-MHz proton nmr spectrum taken in 1,2-dimethoxyethane consisted of one sharp singlet at τ 4.54. This was assigned to the protons on two equivalent cyclopentadienyl rings. The infrared spectrum obtained in a Nujol mull showed characteristic absorptions at 2500 (s), 1015 (s), 905 (m), 890 (m), 850 (s), 840 (s), 745 (m) (cm^{-1} (intensity)). Cyclic voltammetry in dichloromethane demonstrated two reversible reduction waves at −0.27 and −1.35 V. These data are consistent with either the ortho or meta isomer of $(C_5H_5Ni)_2B_{10}H_{10}$. X-Ray crystallography studies are in progress to differentiate between these two possibilities.

The cage opening reaction of $B_{10}H_{10}^{2-}$ with a proton in the presence of ligands to form $B_{10}H_{12}(\text{ligand})_2$ species is thought to involve a nido intermediate.[3] A similiar mechanistic step may initially occur during the reaction of $B_{10}H_{10}^{2-}$ with $(C_5H_5)_3Ni_2^+$. These observations suggest the possibility of synthesizing a large variety of metalloborane species by reaction of closo-borane anions with metal electrophiles, *e.g.*, Π-$C_6(CH_3)_6)_2Co^+$. This and related mechanistic points related to the formation of I and II are under investigation.

Both I and II are water and air stable species, unlike many nido metalloboranes[4,5] previously reported. The compound II can be heated to 350° and subsequently sublimed at 265° over a period of hours with only partial decomposition. Compound I is stable in H_2O_2–H_2O and can be recovered unreacted after boiling several days in ethylene glycol–KOH. These compounds provide pleasing examples of the ability of polyhedral electron counting rules[6-8] to predict, on an *a priori* basis, the existence and relative stability of closo-metalloboranes.[8].

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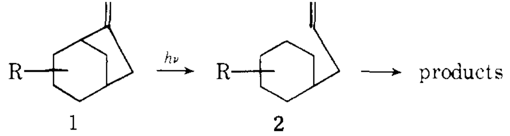
Conformational Control in the Photochemistry of Substituted Bicyclo[3.2.1]octan-6-ones

Sir:

Study of the photochemical α-cleavage of bicyclo[3.2.1]octan-6-ones (**1**) affords an opportunity to examine the conformational behavior of the derived biradical intermediates, **2**.[1,2] There are now many reports of the control of photochemical reactions by ground state conformation,[3-5] along with evidence that changes in conformation may occur specifically in the excited state.[5] There are also good examples of conformational effects on behavior of



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