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Organic Chemistry on the Solid Phase. Site-Site Interactions on Functionalized Polystyrene

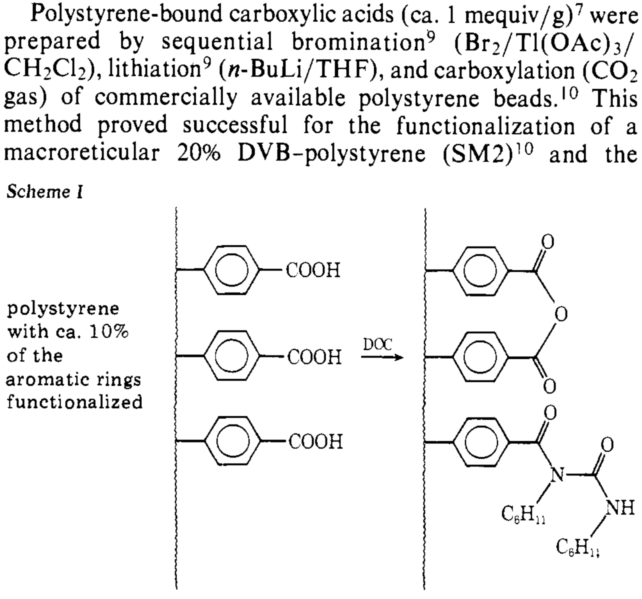
Sir:

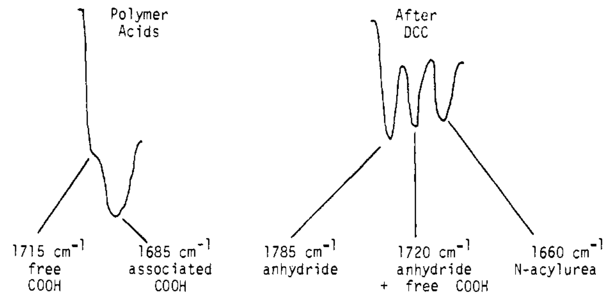
The ability to insulate molecules from one another by attaching them to an inert, rigid matrix could provide a valuable alternative to the high-dilution principle for the supression of undesirable bimolecular reactions in such areas of chemistry as large ring synthesis and the study of highly reactive species. It has often been assumed[1] that the 2% divinylbenzene-styrene copolymer (2% DVB-polystyrene) commonly employed for solid-phase synthesis provides such "matrix isolation"; however, Rapoport and co-workers have demonstrated[2,3] most convincingly that it does not. We have examined the suggestion that more highly cross-linked polymers should provide a more rigid matrix and thereby more effective isolation of functionalized sites.[3] Our findings reveal *significant site-site interaction on functionalized polystyrene, even at high levels of cross-linking.*[4]

As a probe for site-site interaction, a series of polystyrene-bound carboxylic acids was prepared, treated with dicyclohexylcarbodiimide (DCC), and then examined for the presence of anhydride.[5] The extent of anhydride formation in these experiments represents a *lower-limit* of site-site interaction, since the *O*-acylisourea intermediate formed on addition of a carboxylic acid to DCC rearranges to the stable *N*-acylurea unless intercepted by another carboxylic acid[6] (Scheme I).

Polystyrene-bound carboxylic acids (ca. 1 mequiv/g)[7] were prepared by sequential bromination[9] ($Br_2/Tl(OAc)_3/CH_2Cl_2$), lithiation[9] (*n*-BuLi/THF), and carboxylation (CO_2 gas) of commercially available polystyrene beads.[10] This method proved successful for the functionalization of a macroreticular 20% DVB-polystyrene (SM2)[10] and the "swellable" 1, 2, and 4% DVB-polystyrenes (SX1, SX2, and SX4, respectively)[10] but failed[11] with "swellable" 8 and 12% DVB-polystyrenes (SX8 and SX12).[10] The infrared spectra of these carboxylated polymers show carbonyl stretching bands for both free and associated carboxylic acids,[8] the latter band appearing more intense in all cases (Figure 1).

Scheme I





	1715 cm^{-1} free COOH	1685 cm^{-1} associated COOH	1785 cm^{-1} anhydride	1720 cm^{-1} anhydride + free COOH	1660 cm^{-1} N-acylurea
SX1	0.7	1.0	1.0	0.9	0.9
SX2	0.7	1.0	1.0	0.9	0.8
SX4	0.7	1.0	1.0	3.7	3.7
SM2	0.8	1.0	1.0	1.5	1.6

Figure 1. Relative intensities of infrared absorption bands (KBr) for various carboxylated polystyrenes (see text for description) both before and after treatment with DCC. The spectra pictured above the table are for SX2.

Each of the carboxylated polymers was stirred in methylene chloride with excess DCC for 50 h at room temperature.[12] Infrared spectra taken after filtration, washing, and drying are summarized in Figure 1. In all cases, the associated-COOH band (1685 cm^{-1}) disappears, and new bands for anhydride (1785 cm^{-1}) and the *N*-acylurea (1660 cm^{-1}) appear. The second anhydride carbonyl band (ca. 1720 cm^{-1}) unfortunately coincides with that of any remaining free COOH (1715 cm^{-1}). The relative intensities of the band in this region, however, suggest the presence of residual free COOH, which is completely inaccessible to DCC, on the more highly cross-linked polymers (SX4 and SM2).

According to Rapoport et al.[2] the majority of functionalized sites on 2% DVB-polystyrene (SX2, ca. 1 mequiv/g) can interact. Our data show that the extent of site-site interaction on more highly cross-linked polystyrene, although somewhat reduced, still remains significant. Even in the best case we have found (SX4),[10] the number of available, truly insulated sites (<1 mequiv/g) probably falls too far below the practical limit for most applications of organic chemistry on the solid phase.[13]

Note Added in Proof. Resin-bound benzyne (0.23 mmol/g on SX2 and 0.09 mmol/g on SM2) does not "dimerize" but is destroyed by an unknown pathway with a half-life of *ca.* 1 min.[15] This result is in complete agreement with our observation that site-site interaction is time dependent.[12]

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(3) For an excellent, recent review see J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, 135 (1975).
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styrene has been shown to decrease with increased cross-linking (S. L. Regen, *J. Am. Chem. Soc.*, **96**, 5275 (1974)), these elegant experiments do not bear directly on the question of site–site interaction.

(5) This method, although conceived independently by us, closely resembles that used by Rapoport et al. for the study of 2% DVB–polystyrene.[2]

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(7) The extent of functionalization was determined[8] by stirring the carboxylated resins with excess NaOH in aqueous tetrahydrofuran, filtering, washing the beads, and titrating the filtrate with HCl. Combustion analysis both before and after the lithiation–carboxylation gave the bromine content of each sample.

(8) R. L. Letsinger, M. J. Kormet, V. Mahadevan, and D. M. Jerina, *J. Am. Chem. Soc.*, **86**, 5163 (1964).

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(10) BIO-RAD Laboratories, Richmond, Calif. 94804.

(11) Brominated SX8 and SX12 could be prepared without difficulty in the usual manner.[9] Combustion analysis both before and after attempted lithiation,[9] however, revealed that only about 50% of the bromines on SX8 and less than 1% of those on SX12 could be replaced. Added hexamethylphosphoramide did not improve the reaction on SX12 at −10 °C in THF. Presumably *n*-BuLi has difficulty penetrating the more highly cross-linked polystyrene beads. BIO-RAD reports[10] the following molecular weight exclusion limits: SX1(14 000), SX2 (2700), SX4 (1400), SX8 (1000), SX12 (400), and SM2 (14 000).

(12) Shorter times and lower temperatures (2 h at 0 °C) give diminished but detectable amounts of anhydride in all cases.

(13) Low levels of functionalization are practical only for polymer-bound *catalytic* species where each active site can be used many times over, e.g., R. H. Grubbs, C. Gibbons, L. C. Kroll, W. D. Bonds, Jr., and C. H. Brubaker, Jr., *J. Am. Chem. Soc.*, **95**, 2373 (1973); W. D. Bonds, Jr., C. H. Brubaker, Jr., E. S. Chandrasekaran, C. Gibbons, R. H. Grubbs, and L. C. Kroll, *ibid.*, **97**, 2128 (1975).

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A Vanadium Carbonyl Trihydride, $H_3V(CO)_3$diars

Sir:

While noncluster second- and third-row transition metal complexes containing more than two coordinated hydride ligands are now very common, relatively few such first-row transition metal complexes have been reported.[1] The latter are H_4FeL_3 (L = PEt_2Ph and $PBuPh_2$)[2] and H_3CoL_3 (L = various phosphines).[3] We now report that the first polyhydride complex of vanadium, $H_3V(CO)_3$diars (**1**) (diars = *o*-phenylenebis(dimethylarsine)), is formed rapidly and in good yield (60–80%) by the interaction of $[Et_4N][V(CO)_4$diars] (**2**)[4] with excess anhydrous or aqueous HX (X = Cl, Br, I) in tetrahydrofuran (THF). The same substance is also generated more slowly but in higher initial purity from **2** and an excess of *tert*-butyl chloride suspended in water.[5,6] By monitoring infrared spectra in the carbonyl stretching region of these reactions, $HV(CO)_4$diars (**3**)[4] has been shown to initially form. Excess hydrogen chloride then reacts with **3** to generate **1** and phosgene (or CO_2 in the presence of water) in approximately equal amounts.[6] Although the formation of phosgene requires the presence of chloride ion, by varying the reaction components we have determined that a strong acid is also necessary. Thus, **2** or **3** in the presence of neutral water, aqueous NaCl, or Bu_4NCl in THF do not give **1**. Also, moderately strong acids having weakly nucleophilic conjugate bases such as aqueous H_2SO_4 and $H_4PO_{H3}PO_4$ convert **2** to **3** but do not provide **1**. On the basis of having established the requirement of HX (X = Cl, Br, or I) and formation of phosgene[7] during the generation of **1** the following pathway for the reaction is proposed;[8]

$$\begin{aligned} &HV(CO)_4\text{diars} + HX \rightleftharpoons [H_2V(CO)_4\text{diars}^+X^-] \\ &\qquad \rightleftharpoons [HV(CO)_3\text{diars}\,\{C(OH)X\}] \\ &\overset{HX}{\rightleftharpoons} H_2V(CO)_3\text{diars}\,\{C(OH)X_2\} \rightleftharpoons H_3V(CO)_3\text{diars} + COX_2 \\ &\qquad\qquad (X = Cl, Br, I) \end{aligned}$$

Although the overall scheme is unprecedented in metal carbonyl chemistry, the individual steps are consistent with known reactivity patterns of carbonyls.[9] For example, nucleophilic attack of coordinated carbon monoxide by a variety of groups including hydroxide and water[10] are known. Protonation of metal carbonyls also enhances the susceptibility of coordinated carbonyls towards nucleophilic attack.[11] The high coordination number of vanadium in **3** may favor protonation at a carbonyl oxygen rather than the metal center. This latter process may be crucial in permitting facile halide attack resulting in the eventual elimination of phosgene.

The physical and chemical properties of **1**, the first derivative of the unknown trianion $V(CO)_3\text{diars}^{3-}$,[12] are noteworthy. Its infrared solution spectra in THF show two intense and sharp carbonyl stretching frequencies at 1840 and 1779 cm^{-1}, which are at unusually low energy for terminal carbonyls in neutral complexes.[13,14] A strongly temperature-dependent ^1H NMR signal attributable to the hydridic protons is also observed. While the signal is too broad to detect at room temperature,[15,16] a well-defined singlet of relative intensity 3 with respect to the 12 methyl-diars protons is observed at τ 8.86 in CD_2Cl_2 at −20 °C. The signal retains its sharpness down to −70 °C. Compared to most metal hydride chemical shifts, this signal occurs at relatively low field but not unprecedentedly so.[17-20] The diars methyl groups in (I) give rise to a pair of signals of equal area at τ 8.28 and 8.54 in CD_2Cl_2 which do not broaden or coalesce between 25 and −70 °C.

In contrast to other carbonyl hydrides of vanadium,[4,16,21] **1** is quite unreactive and thermally stable.[22] For example, unlike **3**, which is readily deprotonated to form $V(CO)_4\text{diars}^-$,[4] attempts to deprotonate **1** with butyllithium failed to provide any evidence for the formation of $H_{3-n}V(CO)_3\text{diars}^{n-}$ (n = 1, 2, or 3) at −78 °C. Instead, decomposition to uncharacterized species occurred. Although we have been unsuccessful thus far in observing any parallels in the chemistry of **1** and the other known group Vb trihydrides, $M(C_5H_5)_2H_3$ (M = Nb and Ta),[23] the photolysis of **1** with an unfiltered medium-pressure mercury vapor lamp in the presence of carbon monoxide provides substantial yields of **3**.[4] Evidently, a photoinduced elimination of molecular hydrogen from **1** occurs during this process, generating coordinatively unsaturated $HV(CO)_3$diars which is trapped with carbon monoxide to provide the observed product. Similar photochemical processes have been reported recently for $IrClH_2(PPh_3)_3$ and $IrH_3(PPh_3)_3$.[24]

Potentially, the reaction of other metal carbonyls and carbonyl monohydrides with hydrogen halides under similar conditions could be an important general route to transition metal di- and trihydrides. Indeed, we have shown that the treatment of $HV(CO)_4$dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) and $Nb(CO)_4DPPE^-$ (DPPE = 1,2-bis(diphenylphosphino)ethane)[25] with *tert*-butyl chloride and water provides substances which have infrared spectra very similar to that of **1**.[26] However, analogous reactions of HCl or *tert*-butyl chloride–water with related carbonyls give either decomposition, no reaction, or other products: $HV(CO)_4DPPE$[21] (decomposition to VCl_3), $W(CO)_4$diars[27] (no