This is a reasonable result and can be attributed primarily to stabilization of the ionic products by solvation.

This work demonstrates that a wealth of thermochemical data results from quantitative pulsed ICR studies of gas phase reactions and that combination of the gas phase data with solution phase thermochemical data can reveal new insights into the process of solvation. We are currently involved in measuring the gas phase acidities of a wide variety of Brönsted acids.

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Organic Synthesis Involving Multipolymer Reactions. Polymeric Trityllithium^{1,2}

Sir:

The use of polymeric reagents in general organic synthesis has greatly increased in recent years due to a number of distinct advantages these reagents possess over analogous, soluble, low molecular weight reagents. The major advantages are insolubilization and immobilization of the polymer-attached reagent and the possibility of influencing reaction paths by specially tailored polymeric carriers. Several recent articles review this subject exhaustively.3-5

The use of more than a single polymeric reagent in reactions, either simultaneously or consecutively, has been rather limited to date. We have demonstrated the usefulness in certain reactions of attaching two reagents to the same polymer.⁶ An ingenious method for detection of highly reactive intermediates has been developed, using two polymeric reagents simultaneously.7 In another study two homogeneous catalysts were attached both to two mixed polymer batches and to the same batch for effecting consecutive catalytic reactions.8

We have shown previously that two reagents possessing high reactivity toward each other are rendered completely inactive Scheme I

A + B
$$\longrightarrow$$
 Products
(P) - A + (P) - B \longrightarrow no reaction
(P) - A + (P) - B + SH
S - A
(P) = insoluble polymer

A, B, SH = soluble reagents S^- = reactive anion

by their attachment to two insoluble polymer batches, respectively.⁶ In this communication we report on the use of this effect in selective synthetic reactions ("multipolymer reactions"), in which two or more polymeric reagents react indirectly through the mediation of a soluble "messenger" reagent. When the polymers are mixed in a common vessel we term the process a "wolf and lamb" reaction.9 In such reactions both kinetic factors and equilibrium conditions are expected to differ from those prevailing in conventional reactions in solution, or in reactions utilizing a single polymeric reagent. This is due to the unique possibility of imposing close spacial proximity on two reagents highly reactive toward each other.

When the polymers are placed in different, interconnected vessels a "chemical cascade" is formed. Such a system is expected to substantially improve handling convenience and speed of multi-step syntheses, leading possibly to automation of such processes. Some of these advantages are illustrated by the experiments described below.

"Wolf and Lamb" Reactions. A general scheme of the reactions studied is shown in Scheme I.

SH denotes a compound with acidic protons. \bigcirc -B is a polymeric base converting SH into its conjugate base S⁻, which then reacts with an electrophilic polymer O-A to yield the product S-A. In similar reactions in solution, S-A is often obtained in low yield because of side reactions of S⁻ or of S-A.

Previously, it was shown that, by immobilization of a carbon acid on a polymer, the extent of side reactions such as selfcondensations and proton exchange with the products may be diminished.¹⁰ It is shown below that the effect of such competing reactions may be eliminated also by the simultaneous use of two polymeric reagents and a soluble carbon acid.

A novel polymeric reagent, polymeric trityllithium (I), was synthesized for these reactions. It was prepared by Friedel-Crafts alkylation of polystyrene¹¹ by benzhydrol or benzhydryl chloride,¹² followed by reaction of the resulting polymeric triphenylmethane with methyllithium or *n*-butyllithium in THF or in 1,2-dimethoxyethane, as shown in Scheme II.

Loadings of up to 2.3 mmol/g of triphenylmethane moieties were indicated by increase in weight. This agreed well with a loading of 2.2 mmol/g of trityl anion as measured by

Scheme II



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+ $(C_6H_5)_3C^{-}Li^{-}$ CH,COC,H CH₃COC₆H₅ жос.н C₆H₅COCH₂COC₆H₅ CH2COC6H. $C_{e}H_{s}\dot{C}$ = CHCOC_eH₅ + CH₃COC_eH₅

quenching of the deep red polymer I with ethanol and titration with acid. Polymer I is capable of quantitative removal of weakly acidic protons from organic molecules, as demonstrated by the alkylations of 2-methylpropiophenone, 2-methylpropionitrile, and phenylacetylene. The compounds were treated first with excess polymeric trityllithium, and then with methyl iodide or benzyl bromide. Quantitative yields of products were obtained. Thus, 2-methylpropiophenone was converted to 2,2-dimethylpropiophenone and to 2,2-dimethyl-3-phenylpropiophenone, 2-methylpropionitrile was converted to 2,2dimethyl-3-phenylpropionitrile, and phenylacetylene was converted to phenylmethylacetylene.

The following advantages were observed when comparing these reactions with similar reactions of soluble trityllithium: Polymeric triphenylmethane was separated after reactions simply by filtration, yielding usually product of high purity. In reactions with soluble trityllithium, triphenylmethane had to be removed by chromatography, which was time consuming and lowered the yields somewhat. Moreover, the polymer is reusable. Thus, a sample of the polymer was subjected to three repeated loadings by reaction with methyllithium, followed by quenching with ethanol and titration of the ethoxide formed. Successive titrations did not show any appreciable change in loading. The possibility of reusing the polymer compensates for the additional synthetic steps involved in its preparation.

Polymeric trityllithium was then used in a number of "wolf and lamb" reactions, according to Scheme I. For P-A, we used polymeric o-nitrophenyl benzoate. Similar acylating polymers have previously been used in peptide synthesis.¹¹ Polymeric trityllithium could be kept for prolonged periods in intimate mixture with the polymeric active ester (as suspensions in 1,2-dimethoxyethane or THF) without any observable reaction (any reaction would have resulted in discharge of the deep red color of the polymeric base and a change of the white color of the polymeric ester into orange-the color of polymeric nitrophenolate anion). The corresponding soluble compounds were found to react immediately upon mixing.

Upon addition of an enolizable ketone, acetophenone, to the above mixture of polymers, reaction took place immediately, as evidenced by the color changes of the polymers (vide supra). Filtration of the polymers and removal of inorganic salts yielded dibenzoylmethane in 96% yield. The reaction is described in Scheme III.

It was not possible to obtain this product in quantitative yield by a similar reaction of the corresponding soluble reagents, namely the reaction of acetophenone with trityllithium followed by reaction of the resulting enolate with benzoyl chloride



Scheme VI



or o-nitrophenyl benzoate (obviously, an exactly analogous reaction of all three reagents simultaneously is impossible in solution). The yield in this reaction does not exceed 50%, as the product is more acidic than the starting ketone, and acetophenone is re-formed from its anion during the reaction by proton exchange with the product, as shown in Scheme IV. In the multipolymer reaction, however, an excess of polymeric trityllithium may be used so as to convert the reformed acetophenone to its anion, which is further acylated to the product. With soluble reagents, such an excess of trityllithium reacts at a fast rate with the acylating agent, and thus is not effective in driving the reaction to completion.

In a similar manner, high yields were obtained in the acylations of a nitrile and an ester.

Phenylacetonitrile was benzoylated by its addition to a mixture of polymeric trityllithium and polymeric o-nitrophenyl benzoate (Scheme V).

When using the appropriate excess of polymeric reagents, the product was obtained in 94% yield. The highest yield obtained in a similar reaction with soluble reagents was only 45%.

Ethyl phenylacetate was acylated in the same manner, vielding 98% of product, ethyl benzoylphenylacetate. In a control reaction with soluble trityllithium and o-nitrophenyl benzoate, the yield was only 47%.

The two polymers may easily be separated after reaction by selective flotation in chloroform/benzene 1:1. The highly swellable triphenylmethane polymer floats while the nitrophenol polymer precipitates. The polymers thus separated may be dried, reloaded and reused.

Chemical Cascade. This type of reaction sequence was il-

lustrated by combining a "wolf and lamb" reaction, as described above, with a third polymeric reagent, situated in a different vessel. The reaction is described in Scheme VI.

The product of the "wolf and lamb" acylation of acetophenone, dibenzoylmethane anion, was passed without isolation into Amberlyst 15 resin (a macroporous sulfonic acid resin) loaded with hydrazine. A 91% yield of 3,5-diphenylpyrazole (based on acetophenone) was obtained upon filtration of the latter polymer.

Other examples of multipolymer reactions, using additional advantages of these reactions, are being studied at present.

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Protonated Cycloocta[def]fluorenone Dication. A New 14 π -Electron Aromatic System

Sir:

The validity of Huckel's $(4n + 2) \pi$ electron rule for aromaticity¹ has been extensively tested during the past 20 years.² Early attempts to prepare the cyclooctatetraenylium dication 1 (R = H) failed, and only very recently has Olah succeeded in oxidizing 1,3,5,7-tetramethylcyclooctatetraene, thus obtaining the diatropic aromatic dication 1 ($R = CH_3$).³ One of the difficulties in obtaining 1 is the ready formation of the stable homotropylium ion.³ We wish to report the preparation and characterization of the protonated cycloocta[def]fluorenone dication 2(vide supra), a benzannelated derivative of 1 which is stable at room temperature.⁴ The formation of 2 is not accompanied by the formation of any discernible amount of a homotropylium type cation.

Oxidation of cycloocta[def]fluorene⁵ with oxygen in the presence of "Triton B" or in air in the presence of KOH and 18-crown-6 afforded after chromatography 3 (90% yield, mp 126 °C),^{6,7} ν_{max}^{Nujol} (cm⁻¹) 1710 (C=O stretching); *m/e* 231 $(M + 1, 19\%), 230 (M, 74\%), 202 (M - CO, 100\%); \lambda_{max}^{EtOH}$ 237 (*e* 42 000), 295 (12 000), 350 (s) (1050), 430 nm (640); $\lambda_{max}^{HSC} \rightarrow 267 \ (\epsilon \ 20 \ 000), \ 300 \ (s) \ (7200), \ 415 \ (6200), \ 500 \ (s)$ nm (1000) with tailing to longer wavelengths. ¹H NMR $(CDCl_3)^8 \delta^{\dagger}$ ppm 5.79 (s, 4 H, H₄-H₇), 6.90-7.44 (m, 6 H, H_1-H_3 and H_8-H_{10}). Treatment of 3 at -40 °C with "magic acid" (1:1 M FSO₃H-SbF₅) in SO₂ produced a dark red solution. Its ¹H NMR spectrum showed the following bands:⁸



 δ (ppm) 5.23 (d, 1 H, J = 8.0 Hz, H₄), 5.60 (d, 1 H, J = 6.0 Hz, H₇), 6.34 (dd, 1 H, $J_1 = 11.0$, $J_2 = 8.0$ Hz, H₅), 6.76 (dd, 1 H, $J_1 = 11.0$, $J_2 = 6.0$ Hz, H₆), 7.31-7.90 (m, 6 H, aromatic), 12.86 (s, 1 H, OH). The spectrum of this species has been assigned to 4, formed by the protonation of the carbonyl group of 3. It should be noted that the vinylic protons H_4 - H_7 exhibit an ABCD pattern. Elevation of the sample temperature to +31 °C evoked a dramatic change of the ¹H NMR spectrum as follows:⁸ δ (ppm) 8.54 (d, 2 H, J = 8.0 Hz, H₅ and H_6), 8.82 (d, 2 H, J = 8.0 Hz, H_4 and H_7), 8.95–9.50 (m, 6 H, aromatic), 14.61 (s, 1 H, OH). This spectrum did not show any changes within a temperature range of +30 to -50 °C. Neither was it altered after a prolonged stay at room temperature. We attribute the spectrum to 2, a two-electron oxidation product of 4. The presence of the OH proton clearly indicates that the oxidation product 2 did not lose its proton at the carbonyl function. The ¹³C NMR spectrum⁸ of 2 supports this assignment. Although the carbon spectrum of 4 showed 17 bands due to its nonsymmetric configuration, oxidation to 2 resulted in a significant downfield shift and in a much simpler spectrum (nine bands). The total change in carbon chemical shift δC for all 17 carbon atoms in the reaction $4 \rightarrow 2$ is 402 ppm or 201 ppm/e. This value is very near that observed for other dications.9 It should be noted the observed difference in 1H chemical shift between 4 and 2 is 2.6 ppm for the vinylic protons and 1.7 ppm for the aromatic protons. A similar oxidation of the closely related protonated 4,5-methylenphenanthrene ketone, 5,7.10 should yield the nonaromatic protonated doubly charged species 6. This reaction, viz., $5 \rightarrow 6$ affords a probe for the estimation of charge deshielding in 6 vs. charge deshielding and diamagnetic ring current in 2. Treatment of 4,5-methylenephenanthrene ketone at -40 °C with "magic acid" (1:1 M FSO₃H–SbF₅) in SO₂ produced 5, ¹H NMR, δ^8 ppm 7.12 (m, 2 H, aromatic), 7.32 (broad singlet, 2 H, H₉, H₁₀), 7.62 (m, 4 H, aromatic), 12.60 (s, 1 H, OH). Oxidation to the dication occurred upon elevation of the temperature to +31 °C and the following ¹H NMR was observed: δ^8 (ppm) 7.59 (dd, 2 H, J_1 = 7.0, J_2 = 4.0 Hz, H₂, H₇), 8.1 (m, 4 H, aromatic), 8.58 (s,