The thermal stability of this new conformer at temperatures up to 38 °K is explicable if we assume a barrier to interconversion of a few kilocalories per mole. This stability is not unreasonable in view of (a) the results of Bailey and North[13] who measured barriers between trans and cis conformers to be 8.8 ± 1.4 kcal/mol by ultrasonic relaxation techniques, (b) estimates of the resonance energy of esters,[14,15] and (c) of measurements of the double bond character[4,5] (20%) of the C–O bond in methyl formate.

Studies are underway to determine the barrier to interconversion between the two conformers of **1** by measuring interconversion rates in various matrices at higher temperatures.

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Polymer-Protected Reagents. Polystyrene–Aluminum Chloride

Sir:

Insoluble resin techniques offer several advantages in preparative procedures. Resins can be used as diluents to hold reagents from other reagents during a reaction,[1] polymers can be used to hold catalysts during a chemical transformation,[2] and polymers can be used as centers upon which large molecules can be grown.[3-5]

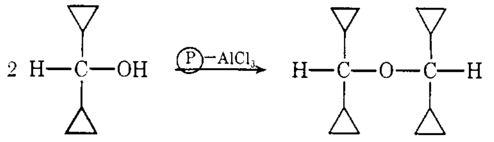
Some time ago, we initiated studies of applications of solid state techniques in organic preparations. In this communication, we report the first use of a tightly bound complex of styrene–divinylbenzene copolymer and anhydrous aluminum chloride, as a mild Lewis acid catalyst for certain organic preparations. The complex of the polymer and $AlCl_3$ provides a shelf-stable acidic material, the active ingredient of which can be called out by an appropriate polymer swelling solvent at the time it is desired.

Polystyrene–divinylbenzene (1.8%) copolymer beads form a water-stable aluminum chloride complex hereafter denoted as Ⓟ–$AlCl_3$. In a typical preparation, 31.0 g (0.46 mol, phenyl residues) of polystyrene–divinylbenzene copolymer beads (1.8%, 50–100 mesh) was added to a 1-l. flask equipped with a stirrer, condenser, and dropping funnel. Carbon disulfide (450 ml) was added followed by 7.5 g (0.06 mol) of anhydrous $AlCl_3$ powder. The mixture was stirred at reflux for 40 min and cooled and 400 ml of cold water was cautiously added to hydrolyze the excess $AlCl_3$. The mixture was stirred until the deep orange color disappeared and the polymer became light yellow. The polymer beads were then filtered and washed with 1 l. of water and successively with 150 ml of ether, acetone, hot isopropyl alcohol, and ether. After these washings, the polymer was dried for 18 hr in a vacuum oven.

Complex formation is demonstrated by the increased color of polymers prepared using higher concentrations of $AlCl_3$, by new bands at 1650 cm^{-1} in the infrared spectrum of the polymer, and by the high general stability of the $AlCl_3$ polymer preparations.[6]

For synthetic purposes, the polymer-bound anhydrous $AlCl_3$ can be released from the polymer by swelling the polymer with certain kinds of solvents. Thus, the $AlCl_3$ can be used to catalyze ether formation and other acid-catalyzed reactions when the polymer holding the reagent is swollen by solvents such as benzene. This is the unique feature of Ⓟ–$AlCl_3$. The polymer protects the easily hydrolyzed Lewis acid until placed in an appropriate solvent where it can be spent in a chemical reaction.

Typical of the reactions of Ⓟ–$AlCl_3$ are its reactions with certain carbinols. For example, dicyclopropylcarbinol, when treated with Ⓟ–$AlCl_3$, produces di(dicyclopropylcarbinyl) ether in yields as high as 81%,[7-9] (eq 1).



(1)

The yield of ether was dependent on the nature of the Ⓟ–$AlCl_3$. The presence of the polymer mediates the effect of the strong Lewis acid catalyst producing higher yields of the desired ether and lower yields of the competing, higher molecular weight side products. In addition, sensitive carbinols react more cleanly with Ⓟ–$AlCl_3$ than they do with $AlCl_3$ directly. Data at 50° for 1:1 mixtures of alcohol and copolymer of different Al content are given in Table I.

The scope of the procedure is demonstrated by the preparation of the mixed ethers, Table II.

Finally, the data in Table III demonstrate the susceptibility of the reaction to the solvent in which the reaction is carried out. Thus, for the reaction of dicyclopropylcarbinol with isopropyl alcohol, much higher product yields are obtained with solvents capable of swelling the polymer. They serve to swell the polymer and make the aluminum chloride more accessible.

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(6) For example, 5 g of Ⓟ–$AlCl_3$ prepared as above but not washed with solvents other than water retained 5.28% Al as the chloride. After washing with 150 ml each of water, ether, acetone, hot isopropyl alcohol, and ether, the polymer retained 3.67% Al as the chloride. The 1650-cm^{-1} band was also retained in the polymer after the above wash procedures. In addition, certain Ⓟ–$AlCl_3$ preparations have been left open to the atmosphere for over 1 year without losing either their catalytic activity or the characteristic infrared bands.

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(9) Di(dicyclopropylcarbinyl) ether was identified on the basis of its spectral properties and confirmed by independent synthesis: nmr δ 2.78 (2 H, t), 1.10–0.20 (20 H, m); ir 9.02 μ; mass spectrum, *m/e* 95 (100%), 111 (13%), 165 (0.1%), 178 (0.1%).

Our conclusion is that polymers may provide extremely useful ways for protecting anhydrous and pyrophoric reagents and attempts are underway to further explore the concept using other reactive reagents. The complete scope of Ⓟ-AlCl$_3$ reactions will be described in a full paper to be published on the work in the near future.

Table I. Product Ratios from the Reaction of Dicyclopropylcarbinol and Ⓟ-AlCl$_3$

% Al in copolymer[a]	Yield of ether,[b] %	% conversion[c]
0	0	0
0.57	74.5	33.1
1.83	64.5	56.8
2.20	58.5	66.5
Pure AlCl$_3$	48.0	75.0

[a] Aluminum analyses by atomic absorption. [b] Analyses after 30 min at 50°. [c] The remainder of the products under these conditions were dimeric and of higher molecular weight.

Table II. Ⓟ-AlCl$_3$ Reactions of Carbinols[a]

Carbinol	Solvent alcohol	Polymer (% Al)	% ether
Dicyclopropylcarbinol	MeOH	0.57	90.4
	EtOH	0.57	65.0
	i-PrOH	0.57	42.5
	t-BuOH	0.57	19.0
Triphenylcarbinol	MeOH	2.20	81.5
	EtOH	2.20	83.0
Diphenylmethylcarbinol	MeOH	2.20	75.8[b]
	EtOH	2.20	59.0[b]
	MeOH	0.57	93.0[b]
Phenyldimethylcarbinol	MeOH	0.57	50.0
tert-Butyl alcohol	MeOH	0.57	0

[a] All reactions were carried out at 60 ± 5° for 90 min. [b] 1,1-Diphenylethylene is the other product.

Table III. Yield of Dicyclopropylcarbinyl Isopropyl Ether as a Function of Solvent Composition[a]

Solvent	Concn of solvent to isopropyl alcohol, wt:wt	Yield of dicyclopropylcarbinyl isopropyl ether, %	Carbinol remaining, %
Hexane	0	57.0	43.0
	1:3	50.1[b]	2.0
	1:1	76.5[b]	2.0
	3:1	80.6[b]	2.0
Benzene	0	57.0	43.0
	1:3	65.0[b]	2.1
	1:1	69.6[b]	1.8
	3:1	81.0[b]	2.0
Carbon disulfide	0	57.0[b]	43.0
	1:3	48.7[b]	2.0
	1:1	77.7[b]	1.7
	3:1	81.4[b]	2.0

[a] All experiments were conducted with polymer containing 0.57% Al. [b] The remainder of the product in these cases was the ring-opened ether.

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(10) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

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Electronic Spectra of 1,1,2,2-Tetramethyl-3,4-benzo-1,2-disilacyclopentene-3 and Related Compounds. Stereoelectronic Verification of σ–π Conjugation between Silicon–Silicon σ Bonds and Benzenoid π Systems

Sir:

In 1964 we,[1] Gilman, *et al.*,[2] and Hague and Prince[3] reported independently that the silicon–silicon bond has conjugating properties with phenyl and vinyl groups. Phenylpentamethyldisilane shows an intense absorption at 43,300 cm^{-1} (ϵ 10,900);[1] the introduction of a pentamethyldisilanyl group into benzene causes a red shift to the extent of 6000 cm^{-1} in the ^1L_a band, whereas the trimethylsilyl group has only a small bathochromic effect on benzene[4] or ethylene.[5] These "conjugating properties" have been rationalized at first in terms of "d–π^*" interaction in the excited state.[1–3,6–8] Later the ground-state interaction between the silicon–silicon σ bond and the π system has been recognized as an important factor in addition to d–π^* interactions. The σ–π interaction has been suggested from the results of uv[9] and charge-transfer[10] spectra. More recently, the photoelectron spectrum has demonstrated that the highest occupied molecular orbital of phenylpentamethyldisilane is a linear combination of σ(SiSi) and π(C$_6$H$_5$) orbitals.[11] We have also indicated the considerable σ-donor character of the silicon–silicon bond in the study of substituent effects on electronic and charge-transfer spectra of phenylpentamethyldisilanes.[12] Currently, σ–π conjugation between the carbon–metal bonds and π systems in the cationic species has been well documented.[13]

In this paper, we show stereoelectronic evidence that provides a strong indication of σ–π conjugation between the silicon–silicon bond and the π system in determining the electronic properties of phenyldisilanes.

1,1,2,2-Tetramethyl-3,4-benzo-1,2-disilacyclopentene-

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