such as **5** is ~15 G which is not at all consistent with the observed $a^{H_\beta}$ of 43.4 G.[12] The similarities in $a^N$ and *g* value for both the cyclic and acyclic sulfonamidyl radicals and the variation and temperature dependence in $a^{H_\beta}$ for R = $CH_2CH_3$ and $CH(CH_3)_2$ reported in Table I for the acyclic sulfonamidyl radicals strongly suggest that these species, likewise, exist in $\pi$ ground electronic state configurations.

The correspondence in ESR parameters, particularly the $a^{H_\beta}$ values for similar R groups, in the aminyl, sulfonamidyl, and amidyl radicals reported in Table II lend considerable support for $\pi$ ground states for all three types of radicals. Although the $CH_3$ groups in these radicals are essentially freely rotating, the $CH_2CH_3$ and $CH(CH_3)_2$ groups attempt to adapt those conformations which minimize steric interactions.[13] As a result of symmetry, there must be an oscillatory motion as discussed in the accompanying paper[5] which is rapid on the ESR time scale so as to render the two $\beta$ hydrogens of the *N*-ethyl radicals equivalent. Compared with the carbonyl group in amidyl radicals, the bulkier $SO_2$ group in sulfonamidyl radicals induces an even stronger repulsive interaction in $CH_3SO_2\dot{N}CH(CH_3)_2$ and $C_6H_5SO_2\dot{N}CH(CH_3)_2$ resulting in small $a^{H_\beta}$ couplings. Even at +60°, $a^{H_\beta}$ is only 10.91 G for the latter radical which is far from the free rotation limit of ~30 G.

In conclusion, the data reported herein, coupled with the variable-temperature studies described in the accompanying paper,[5] should lay to rest any controversy surrounding the ground electronic configuration of sulfonamidyl or amidyl radicals.

**Acknowledgments.** We are grateful to J. Lessard, D. Griller, and K. U. Ingold for communicating their results to us prior to publication. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(12) This reasoning assumes that the relationship $a^{H_\beta} = 59.4 \cos^2 \theta$ applies to such a $\sigma$ radical. Since hyperconjugation is expected to be less important for a $\sigma$ radical, the ~15 G value predicted for **5** is probably a maximum value.

(13) The actual conformation adapted is presumably determined by a relatively complex interplay of steric and electronic effects, the latter including unpaired electron $\pi$ delocalization and hyperconjugation and lone-pair–bond-pair repulsions; steric effects predominate.

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## Stereoselective Syntheses via a Photochemical Template Effect

*Sir:*

Contemporary interest in the use of synthesized polymers in chemical processes has led to many important new developments in solid-phase synthesis.[1-3] Most of the successful applications have used already synthesized polymers as handles in the preparation or separation of organic compounds.[1]

As part of a program designed to take advantage of the properties of polymers in organic processes,[5] we have been investigating the synthesis of polymeric materials which maintain a recognizable macrostructure throughout subsequent photochemical processes. In this communication we describe model studies toward this end and report the synthesis of a series of styrene–divinylbenzene copolymers which not only *recognize their origins*, but which are also able to guide a subsequent photochemical reaction in a specific stereochemical direction. We believe this the first example of a "photochemical template effect".

In principle, the work is based on that of Dickey[6] who demonstrated that silica gel, prepared from sodium silicate and acetic acid in the presence of methyl orange, had a specific affinity for methyl orange in the presence of the ethyl, *n*-propyl and *n*-butyl isomers. More recent work, first by Wulff[7] and later by Shea,[8] has shown that a macromolecule may develop molecular pattern recognitions during its construction based on the monomers from which the macromolecule was constructed—even though the specific molecules of construction no longer remain.

Our goal was to build a polymer with cavities specific for one particular configuration as designated by the three-dimensional structure of an appended small molecule. The question was, would a photochemical reaction carried out in the cavity left after the appended small molecule has been removed from the synthetic polymer lead to a photoproduct with the same geometry as existed in the model compound?[9]

As an example reaction we chose the extensively studied solid-state photodimerization of *trans*-cinnamic acid, the stable crystalline form ($\alpha$) of which gives $\alpha$-truxillic acid and the metastable ($\beta$) form of which produces $\beta$-truxinic acid.[10]

Using methods developed previously[11] to build cavities of specific structure, stereoisomeric $\alpha$-truxillic, $\beta$-truxinic, or $\delta$-truxinic acids were converted into polymerizable monomers. These were then copolymerized with appropriate excesses of styrene and divinylbenzene to form highly cross-linked polymers. Removal of the truxillate or truxinate esters by acidic hydrolysis in methanol left two benzyl alcohol groups in the cavity (Table I, Scheme I).[11]

Treatment of the hydrolyzed polymers **1** with an excess of *trans*-cinnamoyl chloride yielded the polymers **2** (Scheme I). Irradiation of these polymers in degassed benzene suspension[12] produced mixtures of photodimers which could be released from the polymer by acid hydrolysis.

From Table II it is apparent that 53% of the cavities in Ⓟ$_\beta$-**2** specifically synthesize $\beta$-truxinic acid when *trans*-cinnamate is irradiated in a Ⓟ$_\beta$ cavity. Thus, using a polymer synthesized from bis(vinylbenzyl) $\beta$-truxinate the irradiation of the *trans*-cinnamate ester gives 53% $\beta$-truxinate, *even though a randomly synthesized polymer cinnamate ester* would give rise only to $\alpha$-truxillate under identical conditions.[14] The other 47% of the cavities of Ⓟ$_\beta$-**2** give nonspecific direction and hence the formation of $\alpha$-truxillic acid—the expected random product—is observed. $\alpha$-Truxillic acid forms exclusively in Ⓟ$_\alpha$-**2** as is expected since polymeric cinnamate esters,[14] when irradiated in solution, give only $\alpha$-truxillic acid derivatives.

The generality of the concept of the photochemical template effect is demonstrated with a polymer synthesized with bis(vinylbenzyl) $\delta$-truxinate **3**. $\delta$-Truxinic acid[15] is *never*

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**Scheme I**

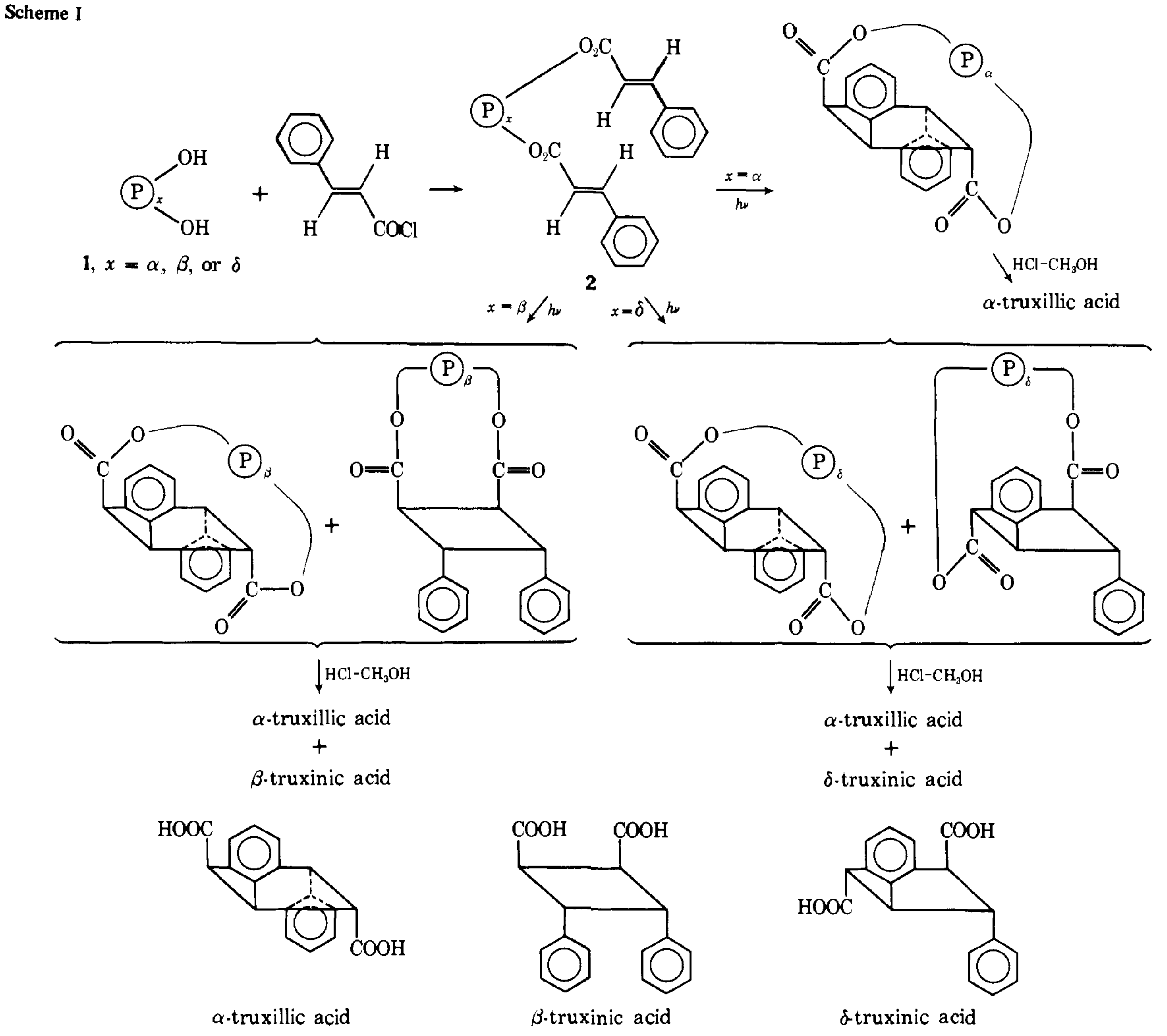


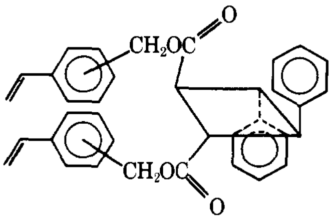
**Table I.** Synthesis of Memory-Containing Vinyl Polymers

| polymer | template monomer X | monomer composition in mol % X | styrene | DVB | %[a] hydrolysis |
|---|---|---|---|---|---|
| Ⓟ$_\alpha$-1 | bis(vinylbenzyl)-α-truxillate | 5.0 | 29.8 | 65.2 | 30 |
| Ⓟ$_\beta$-1 | bis(vinylbenzyl)-β-truxinate | 5.0 | 30.0 | 65.0 | 50 |
| Ⓟ$_\delta$-1 | bis(vinylbenzyl)-δ-truxinate | 4.8 | 45.1 | 50.1 | 30 |

[a] Hydrolysis of the template molecule to completion. No additional truxillate or truxinate ester could be subsequently removed.

formed in the solid-state dimerization of *trans*-cinnamic acid or from its irradiation in solution.

A well-determined amount of hydrolyzed polymer derived from monomer 3[16] was suspended in anhydrous ether and stirred overnight in the presence of excess *trans*-cinnamoyl chloride. After removal of the excess acid chloride and repeated washings with warm dry ether, the polymer was dried in a vacuum oven for 48 h.



3

Irradiation of a mixture of the dry Ⓟ$_\delta$-cinnamate (1 g) and benzene (20 mL) in a Pyrex tube equipped with a magnetic stirrer was carried out on the degassed sample (five consecutive freeze–thaw cycles) for 76 h with a Hanovia 450-W lamp. After irradiation, the tube was broken and the polymer continuously extracted in a Soxhlet extractor—first with toluene and then with MeOH, to remove any soluble material. The washed polymer was then hydrolyzed with MeOH-HCl[11] for 6 h, the polymer was filtered and extracted in a Soxhlet extractor for 24 h, and the filtrates were combined. After the solvents were stripped on a solvent stripper, the combined filtrates were treated with an excess of an ether solution of diazomethane until the yellow color persisted. The resulting methyl esters of δ-truxinic and α-truxillic acid were quantitatively determined by gas chromatography.[11]

The copolymer prepared from bis(vinylbenzyl) δ-truxinate after hydrolysis, conversion into the *trans*-cinnamate ester, irradiation, and another hydrolysis gave esters (52.7%) which

**Table II.** Photochemical Reaction of *trans*-Cinnamate Esters Bound to Polymer Matrices

| polymer | composition of the hydrolysate in mol %[a]<br>$\alpha$-truxillic acid | <br>$\beta$-truxinic acid | <br>$\delta$-truxinic acid |
|---|---|---|---|
| Ⓟ$_\alpha$-**2** | 100 | 0 | 0 |
| Ⓟ$_\beta$-**2** | 47 | 53 | 0 |
| Ⓟ$_\delta$-**2** | 47.3 | 0 | 52.7 |

[a] Note 13.

were derived from $\delta$-truxinic acid. *In other words the polymer matrix directed the photosynthetic event to occur >50% of the time in a stereochemical direction which did not occur at all in monomeric or random polymer analogues.* This result shows that memory-containing polymers can be used to guide the subsequent stereochemical direction of a photochemical reaction. This is a new concept.

This promising observation, coupled with the previously observed memory of a generally synthesized polymer for its chemical origins, suggests many additional ways in which synthesized polymers can be constructed which are selective in subsequent chemical processes. Several of these possibilities are currently under investigation.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported, in part, by the National Science Foundation (DMR78-08493). Helpful discussions with Professor Kenneth Shea and Professor Thomas Kinstle are acknowledged, with gratitude.

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(9) In solution many controls exist which guide photochemical reactions. Two reacting species may be guided by interspersed methylene groups[9a] which control the stereochemical outcome of their photochemical reaction; the multiplicity of the reacting species may be altered;[9b] or the steric bulk of the reacting species may be altered.[9c] In the solid-state reactions are frequently guided by crystal lattice structure.[10] (a) DeSchrijver, F. C.; Boens, N.; Huybrechts, J.; Damen, J.; DeBrackeleire, M. *Pure Appl. Chem.* **1977,** *49*, 237. DeSchrijver, F. C.; Boens, N.; Put, J. *Adv. Photochem.* **1977,** *10*, 359. (b) Griffin, G. W.; O'Connell, E. J. *J. Am. Chem. Soc.* **1962,** *84*, 4148. Zimmerman, H. E.; Durr, H. G. C.; Lewis, R. G.; Bram, S. *Ibid.* **1962,** *84*, 4149. (c) Calas, R.; Lalande, R. *Bull. Soc. Chim. Fr.* **1959,** 763, 766, 770; **1960,** 144, 148. Bouas-Laurent, H.; Calas, R.; Josien, M. L.; Lalande, R. *C.R. Acad. Sci., Ser. C* **1960,** *250*, 4001.

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(11) (a) Unpublished results, J. Damen and D. C. Neckers. The principle method reported herein was developed in several model systems. In one of these, vinylbenzyl-*tert*-Boc-L-proline was copolymerized with styrene and divinylbenzene (10:35:55). After the attached L-proline was hydrolyzed with HBr–CF$_3$COOH, the resulting bromomethyl polymer was treated with racemic *tert*-Boc-proline (Cs salt). Subsequent hydrolysis of the incorporated proline showed it to be enriched in L (L/D = 1.025). This corresponded to a 1.2% enantiomeric excess. We believe this the first example of a "single point", i.e., singly attached, chiral monomer which produced a template in a synthesized polymer. (b) $\alpha$-Truxillic and $\beta$-truxinic acid also generate templates in styrene–divinylbenzene copolymers: J. Damen and D. C. Neckers, *J. Org. Chem.*, in press.

(12) As a solution in degassed benzene, *trans*-cinnamic acid isomerizes—no dimers are observed.[10]

(13) The composition of the hydrolysate was measured by gas chromatography on a 3-ft, $^1/_8$ in. column, filled with 20% Carbowax 20M on Chromosorb W. The acids from the hydrolysate were, prior to GC analysis, converted into their esters by treatment with diazomethane.

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(16) Bis(vinylbenzyl) $\delta$-truxinate was prepared from dipotassium $\delta$-truxinate and vinylbenzyl chloride;[11] copolymerization of the monomer with styrene–divinylbenzene (4.9% monomer; 45.1% styrene; divinylbenzene 50.1%) by polymerization[11] and hydrolysis[11] produced a Ⓟ$_\delta$-**2** with 213 $\mu$equiv of –OH function/g of polymer.

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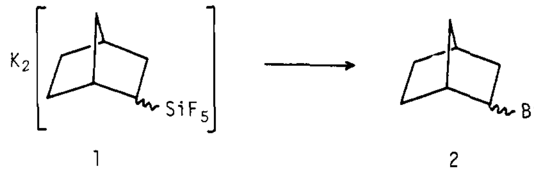
## Stereochemistry at Carbon in Cleavage of the Carbon–Silicon Bond in *exo-* and *endo-*2-Norbornylpentafluorosilicates by Various Brominating Agents[1]

*Sir:*

Electrophilic cleavage of carbon–metal bonds is one of the most important steps in stoichiometric and catalytic organometallic reactions. Much attention has been paid to the stereochemistry of such processes not only to elucidate mechanisms but also to get the basis for many important methods of controlling stereochemistry in organic synthesis.[2] Both retention and inversion of configuration at carbon have been observed.[3,4] Attempts have recently been made to analyze the stereochemistry in terms of initial attack on a HOMO of a metal alkyl.[4b,5] Thus, for $d^0$ and $d^{10}$ systems the HOMO would be a carbon–metal $\sigma$-bonding orbital, while for $d^1$-$d^9$ systems it would be either a nonbonding orbital of essentially d character or a carbon–metal $\sigma$-bonding orbital. Inversion may result from either an $S_E2$ (inversion) mechanism (attack on carbon) or electron transfer (attack on metal) followed by back-side attack by nucleophile, while retention of configuration might result from either an $S_E2$ (retention) mechanism (attack on carbon) or an oxidative addition–reductive elimination sequence (attack on metal). Evidence for the electron-transfer mechanism has been obtained for halogenolysis of organoiron[6] and -cobalt[4c] complexes. For main group organometallics, however, data as yet do not seem to be sufficient and should be accumulated to rationalize the stereochemical courses.

We report here the first stereochemical aspects at carbon in electrophilic intermolecular cleavage of an aliphatic carbon–silicon bond.[7] The alkyl–silicon bond in organopentafluorosilicates readily undergoes oxidative cleavage with various electrophiles which do not affect that in neutral tetracoordinate alkylsilanes.[1,8] On the basis of these novel reactivities, we recently have reported several new synthetic methods[1] including the preparation of organic halides from olefins.[9] We have now determined the stereochemistry of cleavage of the carbon–silicon bond in *exo-* and *endo-*2-norbornylpentafluorosilicates by bromine,[9a,10] *N*-bromosuccinimide (NBS),[9a] and copper(II) bromide.[9b] The first two reactions proceeded with predominant inversion of configuration, while essentially complete stereochemical scrambling was observed in the last.



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