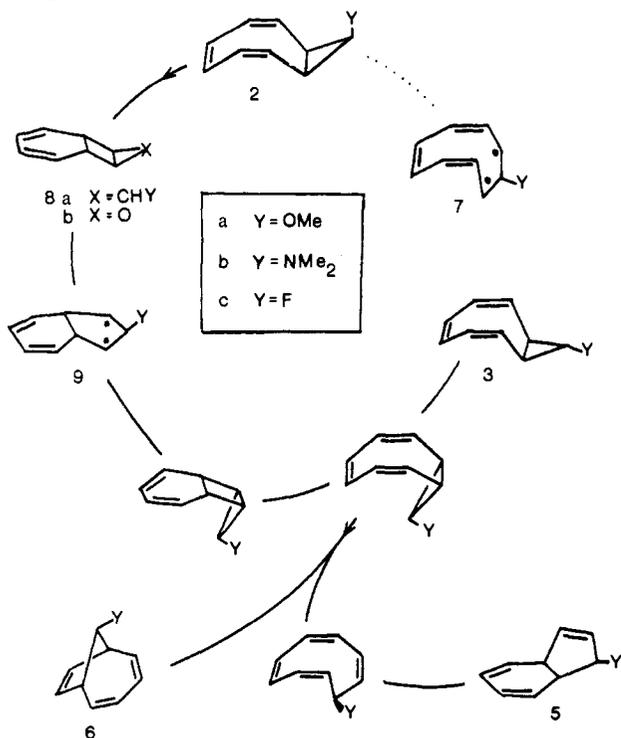


known irreversible thermal rearrangements.⁹ Opening to the biradical **7** with minimal $p\pi$ overlap could in principle be a pathway for epimerization, but this may be energetically inaccessible.¹⁰ An attractive alternative, which we favor, is shown in Scheme I. Tricyclo-

Scheme I



[4.3.0.0⁷.⁹]nona-2,4-dienes have been postulated in the room temperature cycloaddition reaction between bicyclo[6.1.0]nonatriene and hexafluorobut-2-yne^{11a} and in the thermolysis of *syn*-9-chlorobicyclo[6.1.0]nonatriene.^{11b} The closely related compound **8b** is in equilibrium with 9-oxabicyclo[6.1.0]nonatriene at a concentration of 0.4%, the energy barrier for its formation being $\Delta H^\ddagger = 24.8 \text{ kcal mol}^{-1}$ ($\Delta S^\ddagger = -5 \text{ eu}$).¹² The biradical intermediate **9** would be expected to be considerably lower in free energy than **7** (cf. *cis*-hexatriene and 1,3-cyclohexadiene) so that if **8a** is kinetically accessible under conditions of epimerization formation of **9** must be the preferred epimerization pathway. Furthermore, in the postulation of **8a** and **9** the reaction allows rationalization of the observed reactivity order, for epimerization of *syn*-5-methoxybicyclo[2.1.0]pentane^{13a} and related compounds is substantially faster than that of 5-unsub-

stituted bicyclo[2.1.0]pentanes.^{13b} Extended Huckel calculations suggest that epimerization of the corresponding 5,5-difluoro derivative should occur even more readily.^{13c} This facilitation has been ascribed to ground-state destabilization, and to the stabilization of the symmetric biradical state relative to the anti-symmetric state, thereby removing a postulated symmetry crossing in the parent system. A further important factor and indeed possibly the most crucial is the potential for hyperconjugation in the symmetric state of the biradical by mixing of the C-F or C-O bond with the half-filled orbitals by virtue of their high electronegativity and consequent high p character. In addition we note that INDO and *ab initio* calculations on monosubstituted benzenes¹⁴ show that -F and -OMe (but not -NH₂) impart considerable positive charge density to an adjacent carbon atom. Operation of this effect at the center carbon of a 1,3-biradical provides an alternative source of stabilization.

The thermolysis of anti isomers **3b** and **3c** is of further interest, being the first examples of monosubstituted bicyclo[6.1.0]nonatrienes to rearrange to bicyclo[4.2.1]nonatrienes.¹⁵ The stereochemical relationship between **3** and **6** suggests a symmetry-controlled reaction, most probably a [1,5] carbon shift from the folded conformation. There are precedents for facilitation of sigmatropic reactions by amino substitution.¹⁶ The formation of **6c** is surprising, but without further analogies speculative comment is unwarranted.

Acknowledgment. We thank the Science Research Council for a postdoctoral fellowship (to M.M.O) and Mr. A. J. Barnett for preliminary work on **2a**. Professor C. A. Bunton made valuable comments.

(14) W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 1496 (1972); J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

(15) For other carbocyclic examples see A. G. Anastasiou, R. P. Cellura, and E. Ciganeck, *Tetrahedron Lett.*, 5267 (1970); F.-G. Klärner, *ibid.*, 3611 (1971).

(16) F. Scheidt and W. Kirmse, *J. Chem. Soc., Chem. Commun.*, 716 (1972); T. Muiyashi, M. Nitta, and T. Mukai, *J. Amer. Chem. Soc.*, **93**, 3441 (1971); A. P. Ter Borg, E. Razenberg, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **85**, 1230 (1965)

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On the Mobility of Solvent-Swelled Polystyrene Ion Exchange Resins

Sir:

Extensive theoretical and experimental studies have been performed on polystyrene ion exchange resins over the past 20 years.¹ Despite this effort, there still exists only a primitive level of understanding of the molecular mobility associated with the solvent-swelled polymeric chains. We wish to provide evidence which establishes that ion exchange resins derived from 2% cross-linked polystyrene (200–400 mesh) swelled in benzene be-

(1) W. Rieman and H. F. Walton, "Ion Exchange in Analytical Chemistry," Pergamon, New York, N. Y., 1970; J. Inczedy, "Analytical Applications of Ion Exchangers," Pergamon, New York, N. Y., 1966; O. Samuelson, "Ion Exchange Separations in Analytical Chemistry," Wiley, New York, N. Y., 1963; J. A. Marinsky, "Ion Exchange," Marcel Dekker, New York, N. Y., 1966; F. Helfferich, "Ion Exchange," McGraw-Hill, New York, N. Y., 1962.

(9) A. G. Anastasiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Lett.*, 4491 (1969); P. Radlick and A. G. Alford, *J. Amer. Chem. Soc.*, **91**, 6529 (1969); S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969); G. Boche, H. Bohme, and G. Mortens, *Angew. Chem., Int. Ed. Engl.*, **8**, 594 (1969).

(10) The formation of a 1,3 biradical from a 1,2-dialkylcyclopropane is associated with an activation energy of 58 kcal mol⁻¹; cf. R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

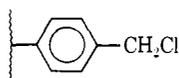
(11) (a) C. S. Baxter and P. J. Garratt, *Tetrahedron*, **27**, 3285 (1971); (b) J. C. Barborak, P. von R. Schleyer, G. Boche, and G. Schneider, *J. Amer. Chem. Soc.*, **93**, 279 (1971). In this latter work, presumably the solvolysis of the 8-chlorotricyclo[4.3.0.0⁷.⁹]nonadiene is too rapid for epimerization to compete.

(12) R. Huisgen, G. Boche, A. Dahmen, and W. Hechtel, *Tetrahedron Lett.*, 5215 (1968).

(13) (a) J. J. Tufariello and A. C. Bayer, *Tetrahedron Lett.*, 3551 (1972); K. Fellenberger, U. Schullkopf, C. A. Bohn, and P. von R. Schleyer, *ibid.*, 359 (1972); (b) J. P. Chesick, *J. Amer. Chem. Soc.*, **82**, 3250 (1960); (c) D. B. Chesnut, S. Ferguson, L. D. Smith, and N. A. Porter, *Tetrahedron Lett.*, 3713 (1972).

have chemically as rigid polymer lattices and that the polymeric chains must have *restricted mobility*.

When chloromethylated polystyrene, **1a**, swelled in benzene, was heated to 70° in the presence of 1 equiv of *N,N,N',N'*-tetramethyl-1,6-hexanediamine (**2a**), chloride ion was displaced at the rate shown in Figure 1.² A maximum of $75 \pm 5\%$ of the chloride was released after 95 hr. The reaction of 1 equiv of diamine **2a** with chloromethylated polystyrene **1b** resulted in the liberation of $66 \pm 2\%$ of the chloride ion after 60 hr. Treatment of benzene-swelled chloromethylated polymer **1a** with 1 equiv of *N,N,N',N'*-tetramethylethylenediamine (**2b**) led to $66 \pm 2\%$ of the chloride ion being



chloromethylated polystyrene-2% divinylbenzene

1a, 1.0 mmol of chlorine/g of polymer
(12% ring substitution)

1b, 0.5 mmol of chlorine/g of polymer
(6% ring substitution)



2a, $n = 6$

2b, $n = 2$

displaced after 20 hr and remained unchanged after an additional 240 hr. When polymer **1b** was treated with 1 equiv of diamine, **2b**, maximum displacement of the chloride ion occurred after 3 hr and was $47 \pm 3\%$. A control experiment in which benzene-swelled polymer **1a** was heated in the absence of either diamine for 280 hr indicated that no detectable chloride ion was displaced ($<1\%$). Thus, by either shortening the distance between the nitrogen atoms of the diamine molecule or by lowering the chloride ion content of the polymer, the relative amount of chloride ion released from the polymer was decreased.

In order to ensure that all of the chloromethylene groups on polymers **1a** and **1b** were active for displacement by tertiary amines of the type used, we treated each polymer with *N,N*-dimethyl-*n*-butylamine employing the same reaction conditions as those for the diamine experiments. We found that this tertiary amine readily liberated 100% of the chlorine from both polymers. When the resulting ion-exchange resins were analyzed for nitrogen, the molar amount of nitrogen bound was identical with the molar amount of chloride ion displaced.⁴

We have determined the molar ratio of bound nitrogen to chloride ion displaced for the reaction of di-

(2) Procedures similar to the one described for the reaction of polymer **1a** with diamine **2a** were followed for all of the systems studied. Chloromethylated polystyrene, **1a** (0.250 g, 0.250 mmol), was placed in a 4-in., 12-mm Pyrex glass tube and was thoroughly degassed under a stream of nitrogen. One milliliter of a benzene solution of diamine **2a** (0.125 M, 0.125 mmol) was added *via* syringe and the tube was sealed under nitrogen, placed in an oil bath maintained at $70 \pm 2^\circ$, and, after a specified time, placed in an ice-water bath to quench the reaction.³ The mixture was quantitatively transferred to a 125-ml erlenmeyer flask with 30 ml of 50% acetic acid, and 5 ml of concentrated nitric acid was added. The amount of chloride ion displaced from the polymer was determined by Volhard titration using procedures described elsewhere: J. M. Stewart and J. D. Young, "Solid Phase Peptide Synthesis," W. H. Freeman, San Francisco, Calif., 1969, p 55.

(3) Benzene was purified by distillation from sodium benzophenone ketyl under a nitrogen atmosphere.

(4) After quaternization was completed, the polymer was thoroughly washed with benzene, ethanol and ether, and was dried under vacuum. The amount of nitrogen bound to the polymer was determined by microanalysis (Midwest Microlab, Indianapolis, Ind.).

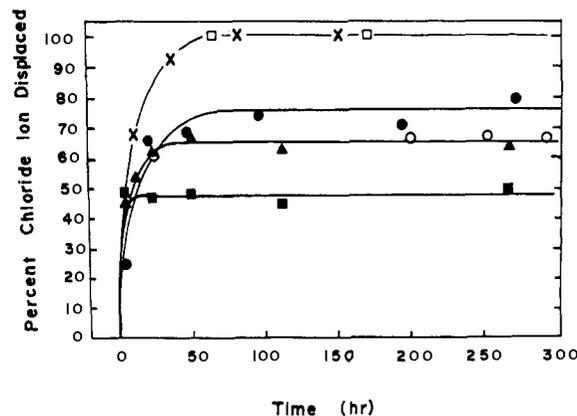


Figure 1. Plot of per cent chloride ion displaced as a function of time for the reaction of **1a** with **2a** (●), **1a** with **2b** (▲), **1b** with **2b** (■), **1b** with **2a** (○), **1a** with *N,N*-dimethyl-*n*-butylamine (□), and **1b** with *N,N*-dimethyl-*n*-butylamine (×).

amine **2b** with polymer **1b** after 260 hr. The ratio observed, 1.9:1, clearly showed that for this system nearly all of the diamine molecules were bound to the polymer by quaternization of only one of the amino groups. In order to test the reactivity of the remaining chloromethylene and amino groups in this polyelectrolyte, we treated a portion of it with 2 equiv of *N,N*-dimethyl-*n*-butylamine for 200 hr and a second portion with 3 equiv of benzyl chloride, also for 200 hr.⁵ Analysis of the resulting mixtures indicated that for both reactions, 100% of the chloride ion was displaced (based on the polymer bound species as being the limiting reagent). Thus, both the remaining chloromethylene and amino groups retained their activity for quaternization.

These results also indicated that the reactivity of the second amino group in **2b** was not significantly reduced because of the proximal positive charge caused by quaternization of the first amino group. Further evidence for this was obtained by allowing **2b** to react with 1 equiv of benzyl chloride under the same conditions used for the polymer reactions. Analysis of the mixture after 12 hr indicated that quantitative quaternization of both amino groups had occurred; *i.e.*, 100% of the chloride ion was displaced. A control experiment carried out for benzyl chloride in the absence of **2b** showed that no detectable chloride was liberated ($<1\%$).

Taken together, these results are consistent only with the assumption that the ion exchange resin has restricted mobility; lowering the chloride ion content of the polymer or shortening the diamine molecule both make fewer chloromethylene groups available for reaction with amino groups covalently bound to the polymer.⁶ Thus, the polystyrene ion exchange resin acts chemically as a rigid lattice.

The reason for the rigidity in these polymeric systems has not been established. Two likely possibilities are

(5) The molar equivalent was based on the amount of unreacted groups on the polymer.

(6) If the polymer were mobile, the second reaction of each diamine molecule could be considered as a normal ring-closure reaction. As such, one might expect that the rate for this process would be significantly lower than the initial polymer amine bond forming step due to an appreciable $\Delta\Delta S^\ddagger$ for the two reactions. By lengthening the chain of the diamine, one should observe even a slower rate of ring closure since, for the larger rings that would necessarily be formed, there would be a lower probability (unfavorable ΔS^\ddagger) for both ends of the molecule to come together. Our results are just the opposite.

(1) there is an intrinsic rigidity of the neutral polymer backbone and/or (2) the rigidity is induced by the clustering of charges.^{7,8} Recent reports dealing with 2% cross-linked polystyryl-diphenylphosphine ligands suggest that the neutral polystyrene framework has sufficient mobility to bring nonadjacent sites together;^{9,10} this would seem to imply that ionic clustering may contribute significantly to polymer rigidity.

We are presently carrying out experiments which will measure the influence of charge clustering on the rigidity of polystyrene ion exchange resins.

Acknowledgment. We are grateful to the Marquette University Committee on Research and Chemistry Department for their financial support and to Michael A. McKinney and a referee for helpful comments.

(7) The clustering of charges in polyelectrolytes can be considered as physical cross-linking.

(8) We treated non-cross-linked chloromethylated polystyrene (6% ring substitution) with 1 equiv of 2b and found that $50 \pm 5\%$ of the chlorine was displaced from the polymer after 70 hr and remained unchanged after an additional 170 hr. Although the molar ratio of bound nitrogen to chloride ion displaced for this reaction was approximately 2.0, a small amount of cross-linking must have taken place since the polymer rapidly precipitated from solution in the form of a gel. Reaction of the original linear chloromethylated polymer with 1 equiv of *N,N*-dimethyl-*n*-butylamine led to quantitative displacement of the chlorine after 20 hr, without the formation of a gel. Conclusions about the effect of ionic clustering on the rigidity of the ion exchange resin cannot be drawn from this set of experiments due to the onset of gel formation.

(9) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Amer. Chem. Soc.*, **94**, 1789 (1972); J. P. Collman and C. A. Reed, *ibid.*, **95**, 2048 (1973).

(10) R. H. Grubbs, C. Gibbons, L. C. Kroll, W. D. Bonds, Jr., and C. H. Brubaker, Jr., *J. Amer. Chem. Soc.*, **95**, 2373 (1973).

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Thiocarbonyl Ylides. Photogeneration, Rearrangement, and Cycloaddition Reactions

Sir:

We wish to report that under nonoxidative conditions,¹ naphthyl vinyl sulfides 1-4 undergo regiospecific photocyclization to thiocarbonyl ylides, e.g., 12. These potentially useful reactive intermediates experience stereospecific hydrogen migration leading to naphtho[2,1-*b*]dihydrothiophenes (5-8). Photogeneration of thiocarbonyl ylides 12 in the presence of a dipolarophile results in cycloaddition to give multicyclic adducts 13-15. This unique ring annelation method which involves the formation of three carbon-carbon bonds and the generation of six centers of chirality in one experimental operation should prove generally useful in the construction of complex ring systems.

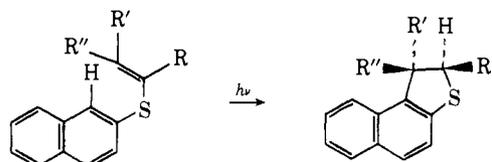
Vinyl sulfides 1-4 were prepared² by the *p*-toluenesulfonic acid catalyzed addition-dehydration of 1 equiv of β -naphthalenethiol to propiophenone (80%

(1) Photocyclization of phenyl vinyl sulfides in the presence of iodine or oxygen to give benzothiophenes in low yield has been reported. However, the mechanistic details as well as the synthetic application of this stilbene-like photocyclization have not been investigated: S. H. Groen, R. M. Kellogg, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968).

(2) E. Campaigne and J. R. Leal, *J. Amer. Chem. Soc.*, **76**, 1272 (1954); R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

yield), 1-indanone (85%), 3-methyl-2-butanone (90%), and phenylacetone (77%), respectively.³

Brief Pyrex-filtered irradiation of 10^{-2} M degassed⁴ benzene solutions of either geometric isomer 1a or 1b leads to photoisomerization about the double bond. Extended irradiation results in consumption of vinyl sulfides and formation of two photoproducts, 5 (15% yield) and 6 (70%). Dihydrothiophenes 5 and 6



1a, R = C₆H₅; R' = CH₃; R'' = H

1b, R = C₆H₅; R' = H; R'' = CH₃

2, R = *o*-C₆H₄CH₂ = R'; R'' = H

3, R = R' = R'' = CH₃

4a, R = CH₃; R' = C₆H₅; R'' = H

4b, R = CH₃; R' = H; R'' = C₆H₅

5, R = CH₃; R' = H; R'' = C₆H₅

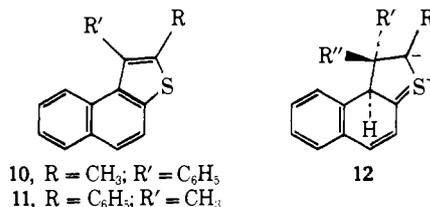
6, R = C₆H₅; R' = CH₃; R'' = H

7, R = R' = R'' = CH₃

8, R = CH₃; R' = C₆H₅; R'' = H

9, R = *o*-C₆H₄CH₂ = R'; R'' = H

undergo dehydrogenation when treated with dichlorodicyanoquinone (DDQ) in refluxing benzene solution to give naphtho[2,1-*b*]thiophenes 10, bp 166-168° at 0.25 Torr, and 11, mp 131°, respectively. Thiophenes 10 and 11 have been unambiguously prepared by polyphosphoric acid cyclodehydration⁵ of the corresponding naphthyl β -keto sulfides.



10, R = CH₃; R' = C₆H₅

11, R = C₆H₅; R' = CH₃

12

The assignment of stereochemistry in dihydrothiophenes 5 and 6 is based on their well-defined and predictable⁶ nmr spectra. Thus, 5 exhibits nonaromatic resonance centered at δ 0.98 (methyl, doublet, $J = 7.0$ Hz), 4.01 (methine adjacent to sulfur, five line multiplet, $J = 7.0$ Hz), and 5.58 (methine, doublet, $J = 7.0$ Hz), while 6 gives resonance at δ 1.53 (methyl, doublet, $J = 7.0$ Hz), 4.15 (methine, eight-line multiplet, $J = 7.0$ Hz and $J = 1.5$ Hz), and 4.45 (methine adjacent to sulfur, doublet, $J = 1.5$ Hz).

Orbital symmetry arguments suggest that cyclization of aryl vinyl sulfides to thiocarbonyl ylides in the photoexcited state will be conrotatory, whereas cyclization from a vibrationally excited ground state will be disrotatory.⁷ Furthermore, stereochemistry of the final product will be fixed if intramolecular hydrogen migration occurs in the intermediate thiocarbonyl ylide. The mode of cyclization in 1 remains uncertain because photoisomerization of 1a and 1b

(3) Satisfactory elemental analyses and spectra compatible with the structural assignments were obtained for all new compounds. All melting points are uncorrected.

(4) Reaction solutions were irradiated in sealed Pyrex tubes degassed by four freeze-pump-thaw cycles with an oil-diffusion-pump vacuum.

(5) O. Dann and M. Kokorudz, *Chem. Ber.*, **91**, 172 (1958).

(6) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970. Cuppen and Laarhoven have shown that photocyclization of α,α' -diethyl-4,4'-stilbenediol occurs via the excited state to give a *trans*-dihydrophenanthrene: Th. J. H. M. Cuppen and W. H. Laarhoven, *J. Amer. Chem. Soc.*, **94**, 5914 (1972), and references cited therein.