8456 *Macromolecules* **2010**, *43*, 8456–8461
DOI: 10.1021/ma1018268

Macromolecules
ARTICLE

Isomerization and Elimination Reactions of Brominated Poly(isobutylene-*co*-isoprene)

Sean M. Malmberg,[‡] J. Scott Parent,[‡] Derek A. Pratt,[†] and Ralph A. Whitney*[,†]

[†]Department of Chemistry and [‡]Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7l 3n6

Received August 10, 2010; Revised Manuscript Received September 16, 2010

ABSTRACT: Brominated butyl rubber (BIIR) is a commercially important value-added elastomer that is produced by solution bromination of butyl rubber to give a microstructure that is predominantly the *exo*-methylene isomer, a kinetic product. It has been demonstrated that isomerization of BIIR to the thermodynamically more stable (E/Z)-endo isomers can be achieved in solution by either electrophilic (zinc stearate) or nucleophilic (tetra-*n*-butylammonium bromide) catalysis without significant formation of conjugated diene through competing elimination, as determined by ^{1}H NMR spectroscopy. Electrophilic catalysis showed little discrimination for (E/Z)-endo isomers of rearranged BIIR, whereas nucleophilic catalysis gave solely the (Z)-endo isomer. The former was interpreted as the result of thermodynamic equilibration, whereas the latter was based on a preferred reactive conformation for S_N2' rearrangement, giving rise to a kinetically preferred product. Computational models supported the interpretation of the experimental results. Rearrangement of BIIR by electrophilic catalysis was also demonstrated in the solid state.

Introduction

Butyl rubber (IIR) is a copolymer of isobutylene with 1−3 wt % of isoprene and is valued for its excellent barrier properties, thermal stability, and resistance to oxidation.[1] Whereas this elastomer can be cross-linked by conventional sulfur, accelerated sulfur, and phenolic resin cure chemistry, the limited unsaturation and slower vulcanization rates of this material result in poor compatibilization with other unsaturated elastomers such as styrene-butadiene rubber (SBR). Consequently, starting in the 1950's, the halogenation of butyl rubber was investigated, with the result that commercial grades of both chlorinated (CIIR) and brominated (BIIR) butyl rubber have been available for over 40 years now.[2] The presence of a halogen accelerates the rate of conventional sulfur cures[3] and allows improved compatibilization with other elastomers such as SBR. Others types of cure chemistry also become available through halogenation of butyl rubber, including amine[4] and zinc oxide cures.[5] The combination of excellent physical properties along with diversity in cure chemistry has led to the application of these materials in a wide variety of products that range from tire inner-linears to pharmaceutical closures.[6]

The microstructure of butyl rubber has been examined in detail by NMR spectroscopy.[7] The isoprene unit is incorporated predominantly as the 1,4-(E)-isomer (**1**) with detectable amounts of the 1,4-(Z)-isomer, as shown in Scheme 1, as well as trace amounts of other structures including those arising from branching. Whereas isomer ratios can vary depending on the process chemistry used, the reported values[7] are typically (≥90):(≤10) for the (E):(Z) ratio. Bromination of butyl rubber is commonly carried out as a solution process using liquid bromine in a saturated hydrocarbon solvent. The reaction proceeds by an unusual electrophilic substitution reaction at the isoprene units rather than addition and can give rise to a variety of isomeric substitution products, as shown in Scheme 1.[8] The process chemistry for this reaction has been refined over the years to allow consistency in controlling the microstructure of BIIR with the consequence that the *exo*-methylene isomer (**2**) is the predominant isomer in commercial products. The minor isomer present is the *endo*-bromomethyl (**3**). The presence of trace amounts of another endo-isomer (**4**) has also been reported in some instances,[6] as has the endo-conjugated diene (**6**),[9] which could be derived from *endo*-**4** by dehydrobromination.

The stoichiometry of the bromination reaction leads to only half the bromine in Br_2 being incorporated into the rubber with the remainder ending up as HBr; however, recent advances in the process chemistry have focused on the subsequent oxidation of HBr to Br_2 to effect higher efficiency in bromine consumption.[10] Additionally the controlled dehydrobromination of BIIR has been investigated[11] to provide conjugated diene butyl (**5** and **6**), which undergoes both peroxide and radiation cross-linking.[6] exo-Conjugated diene butyl (**5**) can also be chemically modified through Diels−Alder chemistry.[12]

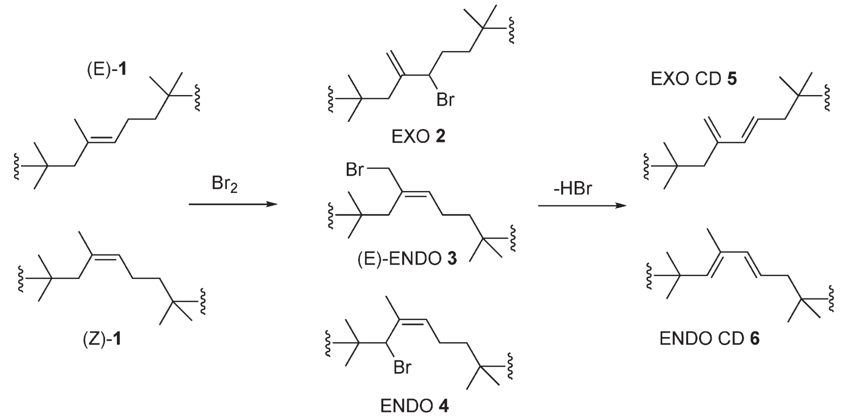
Over the past decade, we have investigated the chemical modification of BIIR with a variety of oxygen, sulfur, nitrogen, and phosphorus nucleophiles.[13−16] During the course of these studies, it has become apparent that there are significant reactivity differences between the exo isomer (**2**) and the (E/Z)-endo isomers (**3**). Consequently it is important to understand how the microstructure of BIIR influences its reactivity. To address this, it is essential to develop methods that allow the isomerization of *exo*-(**2**) to (*E*/*Z*)-*endo*-(**3**) without generating significant amounts of dehydrobromination products (**5** and **6**). The research described herein addresses this issue. Subsequent reports will address the effects of microstructure on the chemical reactivity of BIIR toward chemical modification as well as cure chemistry.

Scheme 2 shows two conceptual strategies for the isomerization of *exo*-(**2**) to (*E*/*Z*)-*endo*-bromomethyl-isomers (**3**). The first of these (path a) involves ionization to an allyl cation, which subsequently recombines by rearrangement; Lewis acid catalysis would be expected to facilitate this pathway. The second strategy

---

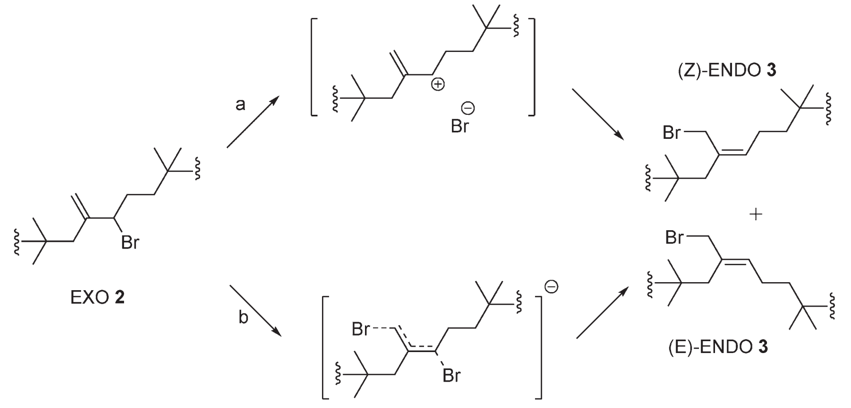
*Corresponding author. Tel: (613) 533-2641. Fax: (613) 533-6669. E-mail whitney@chem.queensu.ca.

Scheme 1. Bromobutyl Isomers and Reaction Product Labelling[a]



[a] Note that (Z)-**1** and (E)-**3** have the same configuration of the double bond; however, changes in the C−I−P priority sequencing due to bromination lead to a change in the stereochemical descriptor.

Scheme 2. Strategies for the Isomerization of *exo*-Bromobutyl to *endo*-Bromobutyl



involves simultaneous bond-making and bond-breaking through an S_N2' process, with bromide ion acting as nucleophile as well as leaving group (path b).

Experimental Section

Instrumentation and Materials. NMR spectra were recorded with a Bruker AVANCE-600 spectrometer (600.17 MHz ^{1}H, 150.92 MHz ^{13}C) in CDCl$_3$, with chemical shifts referenced to tetramethylsilane. Solid-state reactions were done using a Haake Polylab R600 internal batch mixer. The following reagents were used as received from Sigma-Aldrich (Oakville, Ontario): tetra-*n*-butylammonium bromide (TBAB, 98%), 1,8-bis(dimethylamino)naphthalene (99%), magnesium stearate (tech. grade 25% palmitate, 65% stearate); from Fisher Scientific (Ottawa, Ontario): zinc stearate (90%); from Alfa Aesar (Ward Hill, MA): dibutytin dilaurate (94%), iron naphthenate (80% in mineral spirits). BIIR (LANXESS BB2030, $M_n \approx$ 400 000 g/mol, 1.8 wt % Br, ~0.15 mmol/g allylic bromide content) was used as supplied by LANXESS (Sarnia, Ontario).

BIIR Dehydrohalogenation. BIIR (17.5 g, 2.26 mmol allylic bromide), 1,8-bis(dimethylamino)naphthalene (1.46 g, 6.82 mmol), and the desired amount of zinc stearate (none or 0.21 g) were dissolved in xylenes (350 mL) and heated to reflux. Polymer samples withdrawn at intervals were isolated by precipitation from acetone and dried under vacuum. Downfield ^{1}H NMR (CDCl$_3$) analysis: For exo-conjugated diene (**5**): δ 4.76 (s, 1 H, HCH=), 5.04 (s, 1 H, HC**H**=), 5.73 (m, 1 H, −CH$_2$−C**H**=), 6.05 (d, 1 H, H$_2$C=C−C**H**=CH−); For endo-conjugated diene (**6**): δ 5.40 (bs, 1H, −C**H**=C(CH$_3$)−), 5.50 (m, 1 H, CH$_2$−C**H**=), 5.93 (1 H, =C(CH$_3$)−C**H**=).

BIIR Isomerization (Solution). BIIR (1 g) and the desired catalyst (none, 0.12 g zinc stearate or 6.4 mg TBAB) were dissolved in toluene (22 mL) and stirred in an oil bath at 85 °C. Polymer samples withdrawn at intervals were isolated by precipitation from acetone and dried under vacuum. Downfield ^{1}H NMR (CDCl$_3$) analysis: For *exo*-allylic bromide (**2**): δ 5.39 (s, HCH=), 5.02 (s, HC**H**=), 4.40 (t, −C**H**Br−); For (*E*)-*endo*-**3**: δ 5.41 (t, **H**−C=), 4.11 (s, BrC**H$_2$**−); For (*Z*)-*endo*-**3**: δ 5.75 (t, **H**−C=), 4.09 (s, BrC**H$_2$**−).

BIIR Isomerization (Solid State). BIIR (40 g BIIR) was charged to a Haake Rheomix 600 batch mixing bowl equipped with Banbury blades rotating at 60 rpm at a set-point temperature of 85 °C. After 2 min, 0.1 equiv of metal carboxylate salt was added (0.69 g zinc stearate, 0.69 g dibutyltin dilaurate, 0.63 g magnesium stearate, or 0.49 g iron naphthenate in mineral spirits). Samples withdrawn at regular intervals were characterized by ^{1}H NMR spectrum integration to an accuracy of ±5%: δ 5.02 (*exo*-Br, **H**CH=, 1H, s), δ 4.11 (*E*-BrMe, =C−**CH$_2$**−Br, 2H, s), δ 4.09 (*Z*-BrMe, =C−**CH$_2$**−Br, 2H, s).

Computational Methods. The geometries of low energy conformations of two models each of BIIR, its dehydrohalogenation products and its isomerization products and any relevant stereoisomers were determined using the B3LYP gradient-corrected density functional[17] with a 6-31G(d) basis set. Vibrational frequency calculations were carried out to verify the nature of the stationary points as minima on the potential energy surface. Subsequent single-point energies were obtained using the 6-311+G(2d,2p) basis set, and enthalpies and free energies were calculated using these energies combined with the thermochemical corrections obtained in the previous calculation. These data are tabulated along with the relevant geometries in the Supporting

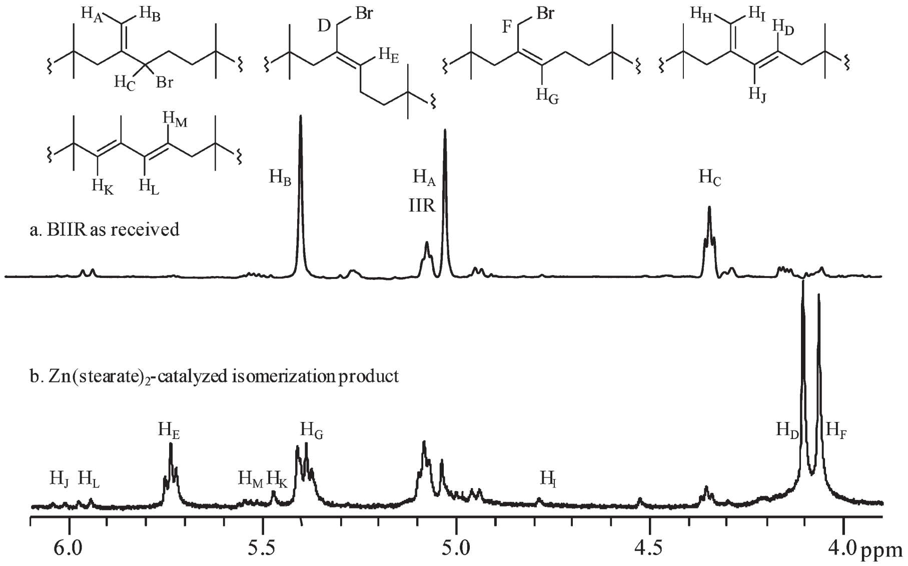


Figure 1. ^1H NMR spectra of brominated butyl rubber: (a) commercial BIIR as received (LANXESS BB2030); (b) zinc stearate isomerized BIIR (solution).

Information. All computations were carried out with the Gaussian 03 suite of programs.[18]

Results

The *exo*-methylene allylic bromide (*exo*-**2**) within commercial BIIR grades is a kinetically favored bromination product that is susceptible to rearrangement to the thermodynamically more stable bromomethyl (*E*/*Z*-*endo* **3**) isomers. The starting material used throughout this work was a commercial grade of BIIR typically containing 0.14 mmol of allylic bromide per gram of rubber, which was distributed in a 90:0:10 ratio of *exo*-**2**/(*Z*)-*endo*-**3**/(*E*)-*endo*-**3**. Small amounts of unbrominated isoprene units were also present, as expected, as well as endo-conjugated diene (**6**) (0.012 mmol per gram of polymer). Figure 1a shows a ^1H NMR spectrum of a commercial grade of BIIR: *exo*-**2** shows singlets at 5.39 and 5.02 ppm and a multiplet at 4.40 ppm; (*E*)- and (*Z*)-*endo*-**3** show singlets at 4.11 and 4.09 ppm, respectively; unbrominated butyl rubber (IIR) shows a multiplet at 5.10 ppm; and traces of endo-conjugated diene **6** are detected by a weak doublet at 5.93 ppm.[12]

BIIR is known to be thermally unstable with respect to the HBr elimination. In the absence of acid scavengers, this leads to degradation of the rubber (145 °C, neat);[9] in the presence of acid scavengers, this leads to the formation of conjugated diene butyl rubber (refluxing xylenes solution, ~135 °C).[12] Isomerization reactions were therefore carried out at significantly lower temperatures to avoid dehydrohalogenation.

Dehydrohalogenation (Solution). When a 5% w/v solution of BIIR in xylenes was refluxed (~135 °C) for 25 h in the presence of an acid scavenger (Proton Sponge, 2.0 equiv per allylic bromide unit), over 80% of *exo*-**2** was converted into exo-conjugated diene (**5**), as evidenced by ^1H NMR. The evolution of reaction products is presented in Figure 2a. The dehydrobrominated products showed no evidence of cross-linking through gel formation, and only the *exo*-(*E*)-conjugated diene (**5**) was generated; the endo-conjugated diene (**6**) is present as a minor component in BIIR (vide supra), and the amount present does not change during the reaction.

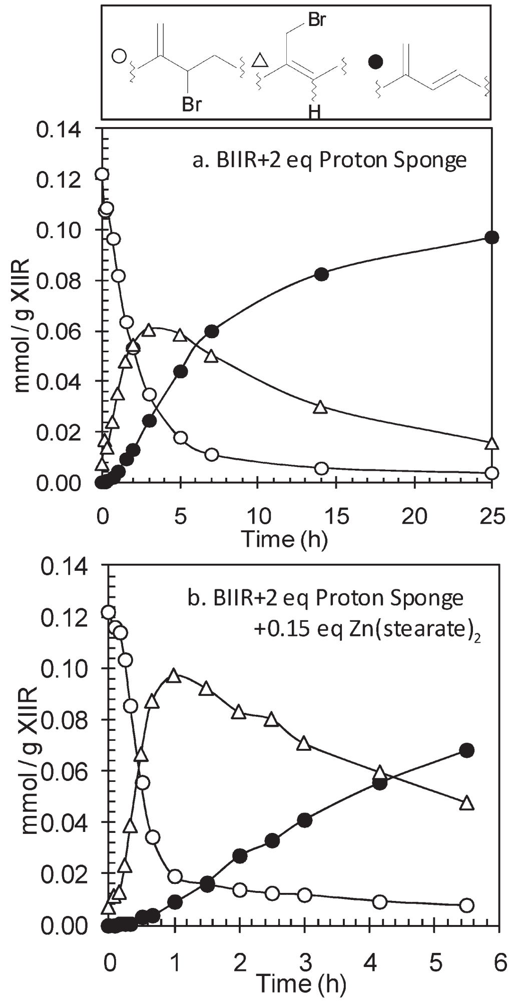


Figure 2. Product evolution for bromobutyl (BIIR) dehydrobromination in xylenes, as determined by ^1H NMR spectroscopy; *T*: refluxing xylenes, 2.0 equiv Proton Sponge. ○, *exo*-**2**; Δ, (*E*/*Z*)-*endo*-**3**; ●, exo-conjugated diene; the amount of endo-conjugated (**6**) is unchanged during the reaction and is omitted from the Figure for clarity.

Because ZnO is routinely used for curing BIIR,[5] the effect of this Lewis acid on the rate of a solution-based dehydrobromination was assessed through reactions employing 0.15 equiv of zinc stearate relative to initial allylic bromide; the concentration of Proton Sponge was held constant at 2 equiv. Figure 2b (which has a different time scale from that of Figure 2a) shows that conjugated diene concentrations

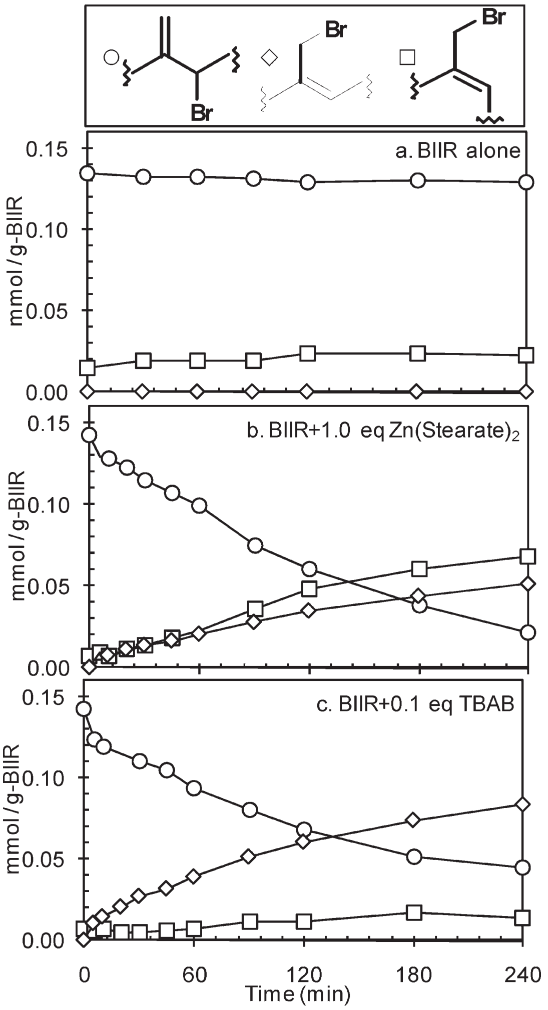


Figure 3. Catalyzed allylic bromide rearrangement (as determined by ^{1}H NMR spectroscopy): (a) bromobutyl (BIIR) alone; (b) BIIR+1.0 equiv Zn(stearate)$_2$; (c) BIIR+0.1 equiv tetrabutylammonium bromide (TBAB) (5 wt % BIIR in toluene, 85 °C). ○, *exo*-**2**; ◇, (*Z*)-*endo*-**3**; □, (*E*)-*endo*-**3**. The amount of endo-conjugated (**6**) is unchanged during the reaction and is omitted from the Figure for clarity.

increased a small amount in the presence of the Lewis acid. After 5 h, the conversion of allylic bromide to exo-conjugated diene was just 34% when no zinc stearate was added but 51% in the presence of zinc stearate (0.15 equiv). More significantly, however, the presence of zinc stearate showed a marked increase in the rate of exo- to (E/Z)-endo isomerization. After 1 h, nearly 80% of the exo isomer had been isomerized with only 10% conversion to exo-conjugated diene. This clearly indicates that isomerization without dehydrohalogenation is a feasible process.

Lewis Acid Catalysis of Isomerization (Solution). Whereas BIIR is stable when maintained at 85 °C in toluene for prolonged periods (Figure 3a), allylic halide rearrangement can be accelerated by treatment with soluble Lewis acids. For example, holding a toluene solution of BIIR with zinc stearate at 85 °C for 4 h gave an isomerized product containing a 10:40:50 ratio of *exo*-**2**/(*Z*)-*endo*-**3**/(*E*)-*endo*-**3** while leaving the total allylic bromide concentration virtually unchanged at 0.14 mmol/g (Figure 3b). The lack of significant (E/Z) selectivity in the collapse of the zinc-coordinated ion-pair intermediate (Scheme 2, path a) suggests that the allyl cation intermediate is formed reversibly (in the forward and reverse directions) and leads to thermodynamic control of products, as discussed below. Figure 1b shows a ^{1}H NMR spectrum of rearranged BIIR: the (*E*)- and (*Z*)-*endo*-**3** show enhanced singlets at 4.11 and 4.09 ppm, respectively; traces of endo- and exo-conjugated dienes **6** and **5** appear as weak doublets at 5.93 and 6.00 ppm, respectively.

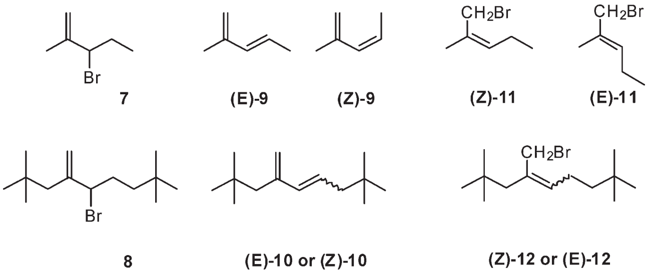


Figure 4. Model structures for computational studies.

Nucleophilic Catalysis of Isomerization (Solution). Figure 3c illustrates the evolution of allylic bromide isomer concentrations when BIIR is exposed to TBAB (0.1 equiv) at 85 °C in toluene. Depletion of *exo*-**2** proceeds smoothly to generate (*Z*)-*endo*-**3** to the exclusion of the corresponding (*E*)-*endo*-**3** isomer. That is, TBAB-catalyzed rearrangement does not yield any (*E*)-endo allylic bromide. This selectivity poses interesting mechanistic questions because it is likely a consequence of a preferred reactive conformation for the S_N2' reaction (Scheme 2, path b), as discussed below.

We noted that TBAB could only engage in an S_N2' rearrangement with *exo*-**2**. A sample of BIIR was isomerized with zinc stearate then purified to give a balanced ratio of (*E*/*Z*)-*endo*-**3** isomers. A subsequent treatment of the isomerized rubber with TBAB (0.1 equiv) in toluene at 85 °C left the isomer ratio unchanged, thereby indicating that TBAB-catalyzed isomerization of *exo*-**2** is an irreversible process.

Computational Studies. The relative energies of two models of BIIR, its dehydrohalogenation products and its isomerization products were explored to help shed some light on the origin of the selectivities in the foregoing transformations. The models feature allylic bromide units of BIIR either truncated at the methylene groups ahead of the quaternary carbons (**7**) or in which the quaternary carbons are included as *t*-butyl groups (**8**). The corresponding models of the dehydrohalogenation products (**9** and **10**) and the isomerization products (**11** and **12**) are also shown in Figure 4. Three-dimensional structures are given in the Supporting Information. Three features of these structures were investigated: the relative stabilities of (E)- and (Z)-exo-conjugated dienes (**9** and **10**), the relative stabilities of the (E)- and (Z)-endo isomers (**11** and **12**), and the torsional energy profiles for rotation about the allylic (=C−CHBr−) bond in **7** and **8**.

The dehydrohalogenation products have a strong preference for the (E) isomers over the (Z) isomers. In the simple model (**9**), the difference is 1.9 or 4.7 kcal/mol depending on whether the s-cis or s-trans conformations of the dienes are considered, of which the latter is highly favored for the (E) but not the (Z). Upon incorporation of the quaternary carbons, the four possible low energy (E) isomers are now favored by a greater margin (2.9−5.0 kcal/mol) over the corresponding (Z) isomers; again, whereas there is a preference for the s-trans conformation in the (E) stereoisomer, there is essentially no preference for either in the (Z).

The computations on the isomerization products reveal a very slight (0.15 kcal/mol) preference for the (E) isomer of both **11** and **12**. The lack of effect of the quaternary carbons on the configurational preference of these products reflects the greater separation of the bulky substituents by the five-carbon planar framework when the double bond is endo as

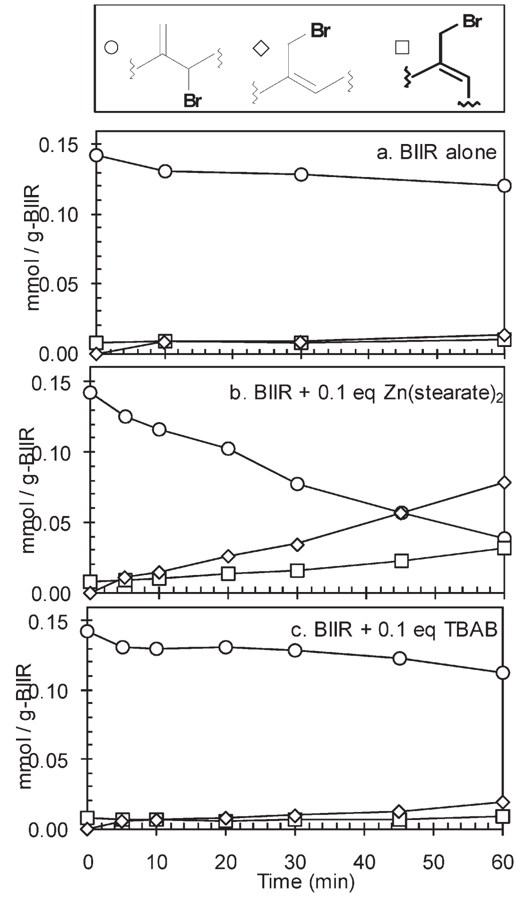


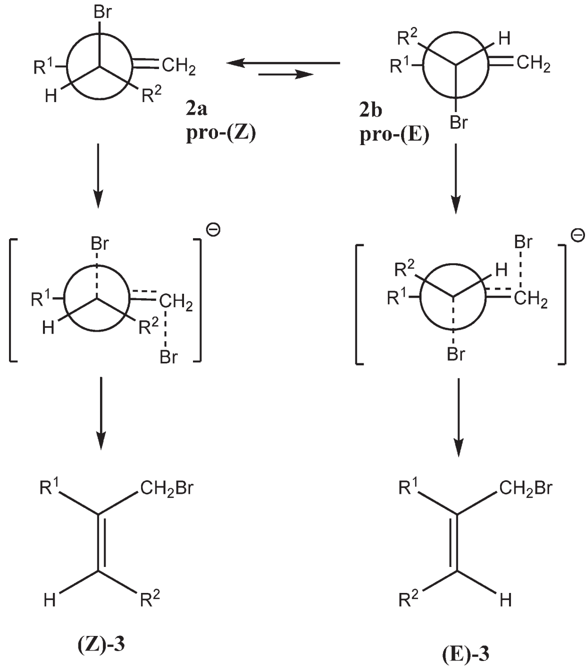
Figure 5. Catalyzed allylic bromide rearrangement in the solid state (as determined by ^{1}H NMR spectroscopy), T = 85 °C: (a) bromobutyl (BIIR) alone; (b) BIIR + 0.1 equiv Zn(stearate)$_2$; (c) BIIR + 0.1 equiv tetrabutylammonium bromide (TBAB). ○, *exo*-**2**; ◇, (*Z*)-*endo*-**3**; □, (*E*)-*endo*-**3**. The amount of endo-conjugated (**6**) is unchanged during the reaction and is omitted from the Figure for clarity.

opposed to the four-carbon planar framework when the double bond is exo in BIIR and its models **7** and **8**.

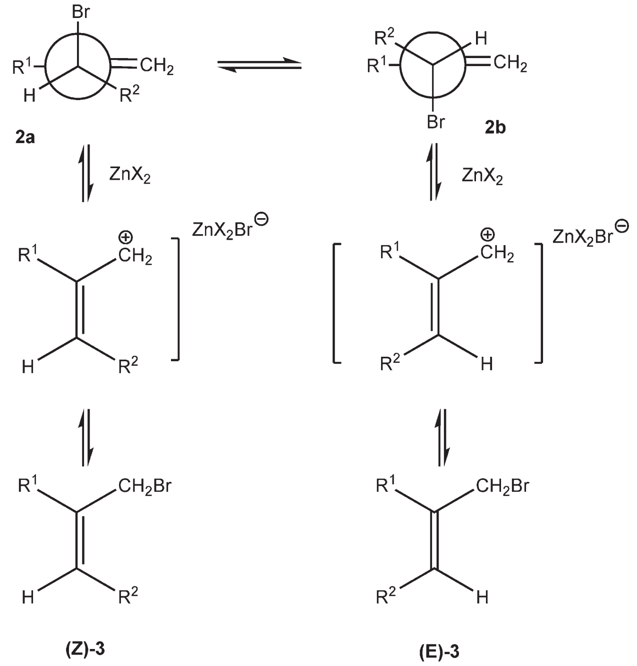
In the case of the simpler model of *exo*-BIIR (**7**), the pro-(E) conformer was favored over the pro-(Z) conformer by 1.0 kcal/mol; the pro-(E) conformer gives rise to (***E***)**-11**, whereas the pro-(Z) isomer gives rise to (***Z***)**-11**. In the case of the more hindered model **8**, however, the order was reversed, with the pro-(Z) conformer favored over the pro-(E) conformer by 4.0 kcal/mol. In both cases, the free energies of activation for interconversion of the conformers were large (cf. 6.6 kcal/mol for *pro*-(*E*)-**7** → *pro*-(*Z*)-**7** and 5.9 kcal/mol for *pro*-(*Z*)-**8** → *pro*-(*E*)-**8**). See the Supporting Information for complete torsional energy profiles for interconversion between the relevant conformers.

Solid-State Isomerization. With isomerization of BIIR having been demonstrated in solution, a solvent-free process was subsequently examined. Experiments were carried out in a batch mixer at 85 °C with the results summarized in Figure 5. Similar to the solution experiments, BIIR alone was stable in the solid state over 1 h at this temperature. The addition of zinc stearate (0.1 equiv, Figure 5b), however, led to a steady conversion of the *exo*-**2** isomer to an (*E*/*Z*)-*endo*-**3** mixture, this time with an excess of the (Z) isomer over the (E) isomer. However, when nucleophilic catalysis of rearrangement was examined with TBAB, surprisingly little isomerization was observed (Figure 5c). This may simply be a consequence of low miscibility of this ionic salt within BIIR as well as the fact that the experiments were conducted below the melting point of TBAB.

Scheme 3. Conformers Leading to an Anti Orientation in the S$_N$2′ Transition State



Scheme 4. Rearrangement by Allyl Cation Intermediates



Following the success of the zinc-stearate-mediated isomerization of BIIR in the solid state, several other Lewis acids were examined for isomerization activity. Both magnesium stearate and dibutyltin dilaurate showed diminished activity relative to zinc stearate, whereas iron naphthenate displayed comparable activity.

Discussion

The dehydrobromination of BIIR to exo-conjugated diene butyl rubber at elevated temperatures has been previously reported.[6,7] Computational studies now indicate that the preferred isomer for this reaction is the (E) isomer (**5**), as shown in

Scheme 1; this result is consistent with the expected reduction of allylic strain in the (E) isomer over the (Z) isomer. Our preliminary results shown in Figure 2 clearly indicate that it is possible to isomerize BIIR with suppression of this elimination reaction.

Nucleophilic catalysis of rearrangement by TBAB is the well-known S_N2' reaction, a concerted allylic rearrangement, which has been extensively investigated from both an experimental[14] and a theoretical[15] perspective. In cases where the nucleophile has a noncoordinating counterion (such as in TBAB), it is generally observed that the reaction proceeds through an anti orientation of nucleophile and leaving group in the transition state rather than a syn orientation. With respect to BIIR, this would require the reaction to proceed through the conformations shown in Scheme 3 (or their mirror images) with the (*Z*)-isomer arising from conformer **2a** (pro-(Z) isomer) and the (E) isomer arising from conformer **2b** (pro-(E) isomer). Conformer **2b** would be expected to have significant nonbonded interactions between R^1 and R^2 ($A_{1,2}$-strain), thereby making it less stable than the conformer **2a**. This is consistent with the experimental results (Figure 2c), which showed that BIIR rearranged exclusively to (*Z*)-*endo*-**3** with TBAB and indicates that this result is likely the consequence of the reaction proceeding through a preferred reactive conformation. This is further supported by the computational results, which showed that the pro-(Z) isomer of structure **8** was 4.0 kcal/mol more stable than the pro-(E) isomer.

Electrophilic catalysis of rearrangement by Lewis acids is expected to proceed via an ion-paired allylic cation, as shown in Scheme 4. Computational results indicated a negligible difference in (E/Z) isomer stability for the model structure **12**, which suggests that an equal mixture of products indicates a process that is under thermodynamic control. The results shown in Figure 3b for solution isomerization with 1 equiv of Lewis acid are consistent with the computational results with a nearly equal mixture of E/Z isomers present. The solid state results showed a greater amount of the (Z) isomer over the (E) isomer; however, these isomerization reactions were carried out for a shorter period of time and at a lower ratio of Lewis acid, so they may simply reflect a system which has not yet achieved equilibrium.

Conclusions

Commercial grades of brominated butyl rubber have a microstructure that consists predominantly of the exo isomer. It has been shown that solution-based rearrangement to the endo isomers can be carried out by either nucleophilic or electrophilic catalysis, with minimal competing dehydrobromination to conjugated diene butyl rubber. The stereochemical outcomes of the these rearrangements can be rationalized on the basis of the conformational preferences of the starting materials and stabilities of the products, which are inferred by the results of computations on models of BIIR and its isomerization products, respectively. Additionally, it has been shown that Lewis-acid-mediated rearrangement can also occur in the solid state. This ability to exercise control of the microstructure of BIIR will allow subsequent comparison of the relative reactivities of exo and endo isomers of BIIR toward chemical modification.

Acknowledgment. The financial assistance of the Natural Sciences and Engineering Research Council and of LANXESS Inc., Sarnia, Ontario, is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates and electronic energies for all optimized structures and torsional potential energy surfaces for structures **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Thomas, R. M.; Lightbown, I. E.; Sparks, W. J.; Frolich, P. K.; Murphee, E. V. *Ind. Eng. Chem.* **1940**, *32*, 1283–1292.

(2) Baldwin, F. P. *Rubber Chem. Technol.* **1979**, *52*, 77–84.

(3) Parent, J. S.; White, G. D. F.; Thom, D.; Whitney, R. A.; Hopkins, W. *J. Polym. Sci., Part A: Poly. Chem.* **2003**, *41*, 1915–1926.

(4) Parent, J. S.; White, G. D. F.; Thom, D.; Whitney, R. A.; Hopkins, W. *Macromolecules* **2002**, *35*, 3374–3379.

(5) (a) Vukov, R. *Rubber Chem. Technol.* **1984**, *57*, 284–290. (b) Henrikse, K. G.; McGill, W. J. *J. Appl. Polym. Sci.* **2000**, *78*, 2302–2310.

(6) http://onlinelibrary.wiley.com/doi/10.1002/0471238961.0221202-511180519.a01.pub2/full, accessed September 30, 2010.

(7) (a) Chu, C. Y.; Vukov, R. *Macromolecules* **1985**, *18*, 1423–1430. (b) Cheng, D. M.; Gardiner, I. J.; Wang, H. C.; Frederick, C. B.; Dekmezian, A. H. *Rubber Chem. Technol.* **1990**, *63*, 265–275. (c) White, J. L.; Shaffer, T. D.; Ruff, C. J.; Cross, J. P. *Macromolecules* **1995**, *28*, 3290–3300.

(8) Chu, C. Y.; Watson, K. N.; Vukov, R. *Rubber Chem. Technol.* **1987**, *60*, 636–646.

(9) Parent, J. S.; Thom, D. J.; White, G.; Whitney, R. A.; Hopkins, W. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2019–2026.

(10) Kaszas, G. *Rubber Chem. Technol.* **2000**, *73*, 356–365.

(11) Baldwin, F. P.; Rac, J. A. Polymers with Conjugated Double Bonds. U.S. Patent 4,068,051, 1978.

(12) MacLean, J. A.; Guillen-Castellanos, S. A.; Parent, J. S.; Whitney, R. A.; Resendes, R. *Eur. Polym. J.* **2007**, *43*, 4619–4627.

(13) (a) Guillen-Castellanos, S. A.; Parent, J. S.; Whitney, R. A. *Macromolecules* **2006**, *39*, 2514–2520. (b) Guillen-Castellanos, S. A.; Parent, J. S.; Whitney, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 983–992.

(14) (a) Parent, J. S.; White, G. D. F.; Whitney, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2937–2944. (b) Parent, J. S.; White, G. D. F.; Thom, D. J.; Whitney, R. A.; Hopkins, W. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1915–1926.

(15) (a) Parent, J. S.; White, G. D. F.; Whitney, R. A. *Macromolecules* **2002**, *35*, 3374–3379. (b) Whitney, R. A.; Penciu, A.; Parent, J. S.; Resendes, R.; Hopkins, W. *Macromolecules* **2005**, *38*, 4625–4629. (c) Parent, J. S.; Liskova, A.; Whitney, R. A.; Resendes, R. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5671–5679.

(16) Parent, J. S.; Penciu, A.; Guillen Castellanos, S. A.; Liskova, A.; Whitney, R. A. *Macromolecules* **2004**, *37*, 7477–7483.

(17) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O. A., A., J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V. C., Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc: Wallingford, CT, 2004.

(19) (a) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901–1930. (b) Paquette, L. A.; Stirling, C. J. M. *Tetrahedron* **1992**, *48*, 7383–7423.

(20) (a) Park, Y. S.; Kim, C. K.; Lee, B.-S.; Lee, I. *J. Phys. Chem.* **1995**, *99*, 13103–10108. (b) Kormos, B. L.; Cramer, C. J. *J. Org. Chem.* **2003**, *68*, 6375–6386. (c) Streitwieser, A.; Jayasree, E. G.; Hasanayn, F.; Leung, S.S.-H. *J. Org. Chem.* **2008**, *73*, 9426–9434.