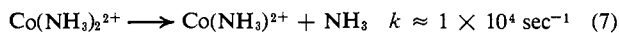


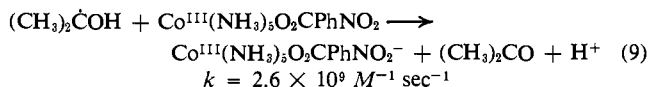
**Figure 2.** Pulse radiolysis of  $5 \times 10^{-4} M$   $\text{Co}(\text{NH}_3)_5\text{O}_2\text{CPhNO}_2^{2+}$  (PNAP):  $0.1 M$  *t*-BuOH, pH 4.3, Ar purged. Conductivity changes following the reduction of PNAP by  $e_{\text{aq}}$  and subsequent decomposition of reduced intermediates.

The next three steps are considerably slower



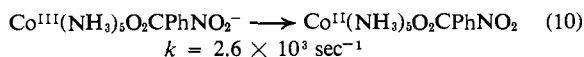
The last rate constant (8) agrees very well with the value  $k = 1.1 \times 10^3 \text{ sec}^{-1}$  (for  $20^\circ$ ) measured by the temperature jump method.<sup>7</sup> (In all the equations the  $\text{H}_2\text{O}$  ligands that replace the  $\text{NH}_3$  are omitted for getting easier formulas.) Similar kinetics were observed for  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ , where the elimination of  $\text{Cl}^-$  and  $2\text{NH}_3$  was very fast, followed by the reactions 6–8.

Using the ac conductivity technique we have also examined the reduction of the cobalt(III) *p*-nitrobenzoato-pentaamine, PNAP, complex which exhibits an interesting primary reduction step of the *p*-nitrobenzoate ligand.<sup>8–10</sup> With isopropyl alcohol radicals as the sole reducing agents ( $\text{N}_2\text{O}$  saturated aqueous solutions of  $0.2 M$   $(\text{CH}_3)_2\text{CHOH}$  and  $5 \times 10^{-4} M$  PNAP, at pH 4.5) the following reaction takes place quantitatively<sup>8</sup>



(For the sake of clarity the charge on the metal center and the carboxylate group are not indicated.) At this stage elimination of ammonia cannot be observed in accordance with the stability of the  $\text{Co}(\text{III})$  complexes.

At pH  $>4$  the extra electron is subsequently transferred intramolecularly from the *p*-nitrobenzoato ligand to the metal center.<sup>8</sup>



The reduced complex is labile and swiftly decomposes. Since the detachment of ammonia is faster than reaction 10, the latter reaction is the rate determining step, and the decrease in conductivity (reaction 4) closely follows the optical decay at 330 nm (reaction 10). Certain lag is present due to the slow elimination of the last ammonia ligand.

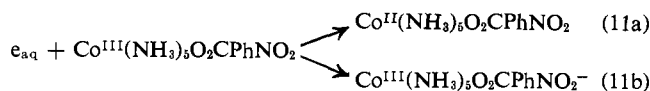
When the hydrated electron is used as the reducing agent the reduction mechanism is somewhat different.

(7) D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

(8) M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, **94**, 1757 (1972).

(9) M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, **92**, 5533 (1970).

(10) E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2987 (1966).



The product of reaction 11a is unstable and decays rapidly (similar to the decay of  $\text{Co}(\text{NH}_3)_6^{2+}$ , Figure 1). This initial decay is evident in Figure 2 and is clearly distinguishable from the much slower one. The intermediate from reaction 11b behaves as described above with reaction 10 as the rate determining step. It is of interest to note the difference in reducing mechanism between  $e_{\text{aq}}$  and other reducing radicals such as  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  and  $\text{CO}_2^-$ . Reactions 11a and b have a 0.3 and 0.7 probability, respectively, as determined by the optical method<sup>11</sup> and the present experiments are a direct proof of that observation.

In conclusion, the described technique is particularly sensitive and can be exploited for the measurements of decay rates of various unstable metal complexes (produced on rapid reduction by hydrated electrons) which are associated with the change in the state of protonation of the freed ligands.

**Acknowledgment.** We thank Dr. A. Henglein for interest and support and Dr. M. Z. Hoffman for kindly supplying the complexes.

(11) M. Simic and M. Z. Hoffman, submitted for publication.

M. Simic

Laboratory of Radiation Biology  
Zoology Department, University of Texas  
Austin, Texas 78712

J. Lilie\*

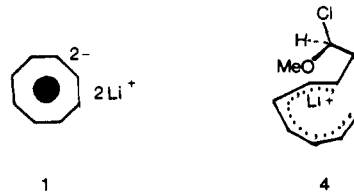
Bereich Strahlenchemie  
Hahn-Meitner-Institut für Kernforschung, Berlin GmbH  
1 Berlin 39, Germany

Received September 11, 1973

### Relative Ease of Epimerization of *syn*-9-Fluoro-, *syn*-9-Methoxy-, and *syn*-9-Dimethylaminobicyclo[6.1.0]nonatriene

Sir:

In contrast to the stereoselective formation of anti-9-substituted bicyclo[6.1.0]nonatrienes in the reaction of dipotassium cyclooctatetraenide with *gem*-dihalo compounds,<sup>1</sup> we have found that the dilithium salt (**1**) may direct reaction to preferential production of *syn* isomer. For example, addition of 1,1-dichlorodimethyl ether to a solution of **1** in  $\text{Me}_2\text{O}$  at  $-80^\circ$  gave rise to 73% *syn* isomer (**2a**) and 27% anti isomer (**3a**). The trends in product ratio (less *syn* isomer with a more basic ether solvent or at higher temperatures) serve to suggest that the reversal of stereochemistry is brought about by intramolecular coordination of methoxyl to the small, hard lithium cation in intermediate **4**. There are precedents for expecting sub-



(1) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964); A. G. Anastassiou and R. C. Griffith, *ibid.*, **95**, 2399 (1973).

stantial binding of lithium ions to an oxygen lone pair under circumstances where potassium ion binding is unimportant.<sup>2</sup> In similar manner **1** reacted with 1,1-dimethoxytrimethylamine in ether at 0° to give a 60:40 mixture of *syn*- and *anti*-9-dimethylaminobicyclo[6.1.0]nonatriene, **2b** and **3b**, respectively. Lithium ion binding to fluorine appears not to operate, for reaction of **1** in Et<sub>2</sub>O with dichlorofluoromethane at -78° gave rise to a 25:75 mixture of *syn*- and *anti*-9-fluorobicyclo[6.1.0]nonatriene, **2c** and **3c**, respectively. With the exception of **2c** all compounds were obtained pure by preparative thin-layer chromatography and fractional distillation.<sup>3</sup> The lability of **2c** precluded isolation of a pure sample although selective rearrangement of **3c** in the mixture on alumina chromatography at 0° allowed the preparation of an isomerically pure sample of **2c** contaminated with 30% indene.

The most striking property of **2a** was its propensity for thermal rearrangement to the equilibrium mixture with **3a** (10:90) observable on standing at room temperature. Good first-order kinetics for this process were obtained by nmr monitoring of the respective -OMe resonances in C<sub>6</sub>D<sub>6</sub>, giving<sup>4</sup>  $k_1$  (323°) =  $2.2 \times 10^{-5}$  sec<sup>-1</sup>,  $k_1$  (331°) =  $6.2 \times 10^{-5}$  sec<sup>-1</sup>,  $k_1$  (338°) =  $1.2 \times 10^{-4}$  sec<sup>-1</sup>, and  $k_1$  (343°) =  $2.4 \times 10^{-4}$  sec<sup>-1</sup>, and therefore  $\Delta H^\ddagger$  = 25.0 ± 1.1 kcal mol<sup>-1</sup> and  $\Delta S^\ddagger$  = 2.37 ± 3.19 eu. In acetone-*d*<sub>6</sub>  $k_1$  (331°) =  $4.4 \times 10^{-5}$  sec<sup>-1</sup>. The rearrangement of **3a** to the corresponding dihydroindene **5a**, accompanied by 10% of a minor product, is much slower but solvent sensitive, for  $k_1'$  (331°) =  $1.98 \times 10^{-6}$  sec<sup>-1</sup> in C<sub>6</sub>D<sub>6</sub> and  $k_1'$  (331°) =  $1.61 \times 10^{-5}$  in acetone-*d*<sub>6</sub>. No rearrangement of **2b** to **3b** could be detected on standing at 70° in C<sub>6</sub>D<sub>6</sub> although thermolysis proceeded ( $k_1$  =  $6.8 \times 10^{-6}$  sec<sup>-1</sup>) to give a 40:60 mixture of **5b** and **6b** with <5% of minor products. Under the same conditions **3b** gave rise to an identical product mixture rather more rapidly ( $k_1$  =  $6.4 \times 10^{-5}$  sec<sup>-1</sup>). It has been clearly established<sup>1b,5</sup> that in the absence of

(2) W. T. Ford, *J. Amer. Chem. Soc.*, **92**, 2857 (1970); D. H. Hunter and D. J. Shearing, *ibid.*, **93**, 2348 (1971).

(3) All compounds reported herein were colorless oils with nmr, uv, and high resolution mass spectra in accord with proposed structures. Pertinent data: **2a** nmr (60 MHz, CCl<sub>4</sub>) δ 5.92, 5.71 (4 H, AB q, H<sub>2,3,6,7</sub>, J<sub>2,3</sub> = 12 Hz), 5.75 (2 H, bs, H<sub>4,5</sub>), 3.38 (3 H, s, OMe), 3.26 (1 H, t, H<sub>9</sub>, J<sub>8,9</sub> = 6 Hz), 1.38 (2 H, d, H<sub>1,8</sub>) ppm; **2b** nmr (60 MHz, CCl<sub>4</sub>) δ 6.10, 5.88 (4 H, AB q, H<sub>2,3,6,7</sub>, J<sub>2,3</sub> = 12 Hz), 6.04 (2 H, bs, H<sub>4,5</sub>), 2.38 (6 H, s, NMe<sub>2</sub>), 1.87 (1 H, t, H<sub>9</sub>, J<sub>8,9</sub> = 6 Hz), 1.39 (2 H, d, H<sub>1,8</sub>); **2c** (60 MHz, CCl<sub>4</sub>) δ 6.1–5.5 (6 H, m, H<sub>2–7</sub>), 4.59 (1 H, dt, H<sub>9</sub>, J<sub>8,9</sub> = 6 Hz, J<sub>9,19F</sub> = 68 Hz), 1.43 (2 H, dd, H<sub>1,8</sub>, J<sub>1,19F</sub> = 8 Hz) ppm; δ<sup>19F</sup> +200 ppm (relative to CFCls); **3b** nmr (60 MHz, CCl<sub>4</sub>) δ 5.88 (4 H, bs, H<sub>2,3,6,7</sub>), 5.78 (2 H, bs, H<sub>4,5</sub>), 2.38 (6 H, s, NMe<sub>2</sub>), 1.55 (2 H, d, H<sub>1,8</sub>, J<sub>8,9</sub> = 4 Hz), 1.18 (1 H, t, H<sub>9</sub>) ppm; **3c** (60 MHz, CCl<sub>4</sub>) 5.95 (4 H, brs, H<sub>2,3,6,7</sub>), 5.82 (2 H, br s, H<sub>4,5</sub>), 3.92 (1 H, dt, H<sub>9</sub>, J<sub>8,9</sub> = 3 Hz, J<sub>9,19F</sub> = 22 Hz) ppm; δ<sup>19F</sup> +188 ppm (relative to CFCls); **5a** uv [EtOH] 261, 272 nm (ε 4200, 4050); nmr (60 MHz, CCl<sub>4</sub>) δ 6.0–5.5 (6 H, bm, H<sub>2,3,4,5,7,8</sub>) 4.37 (1 H, bm, H<sub>9</sub>) 3.68 (1 H, bd, H<sub>1</sub>, J<sub>1,8</sub> = 12 Hz), 3.28 (3 H, s, OMe), 2.85 (1 H, bd, H<sub>8</sub>) ppm; **5b** uv [EtOH] 263, 271 nm (ε 4520, 4560); nmr (CDCl<sub>3</sub>, 90 MHz) 5.73 (2 H, bm) overlapping with 5.56 (4 H, bm, H<sub>2,3,4,5,7,8</sub>), 3.66 (1 H, bs, H<sub>9</sub>), 3.55 (1 H, bd, H<sub>1</sub>), 2.95 (1 H, ddd, H<sub>6</sub>, J<sub>1,8</sub> = 12 Hz, J<sub>6,9</sub> = 5 Hz, J<sub>6,19F</sub> = 3 Hz), 2.19 (6 H, s, NMe<sub>2</sub>) ppm; **6b** uv [EtOH] 249 (sh), 257 (ε 4000), 264 sh, 312 (ε 500); nmr (CDCl<sub>3</sub>, 90 MHz) δ 5.94 (4 H, m, H<sub>2,3,4,5</sub>), 5.16 (2 H, d, H<sub>7,8</sub>, J<sub>1,8</sub> = 1.5 Hz), 2.95 (2 H, bt, H<sub>1,8</sub>, J<sub>1,2</sub> = 5 Hz), 2.22 (1 H, t, H<sub>9</sub>, J<sub>1,9</sub> = 5.5 Hz), 2.05 (6 H, s, NMe<sub>2</sub>) ppm; **6c** uv [CHCl<sub>3</sub>] 258, 267, 275 (ε 4200, 3950, 2450); nmr (90 MHz, CDCl<sub>3</sub>) 5.90 (4 H, brm, H<sub>2,3,4,5</sub>), 5.12 (2 H, dd, H<sub>7,8</sub>, J<sub>1,8</sub> = 2 Hz, J<sub>8,19F</sub> = 3.5 Hz (W-coupling), 5.13 (1 H, dt, H<sub>9</sub>), J<sub>1,9</sub> = 6 Hz, J<sub>8,19F</sub> = 53 Hz), 3.11 (2 H, brt, H<sub>1,8</sub>) ppm.

(4) Bath temperatures are quoted ± 0.2°.  $k_1 \approx k_{\text{obsd}} - k_{-1}$  for decay of **2a** methoxyl signal. The **2a**:**3a** equilibrium ratio was not measurably temperature dependent.

(5) A. G. Anastassiou and R. C. Griffith, *Chem. Commun.*, 1301 (1971); P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, **91**, 1580 (1969).

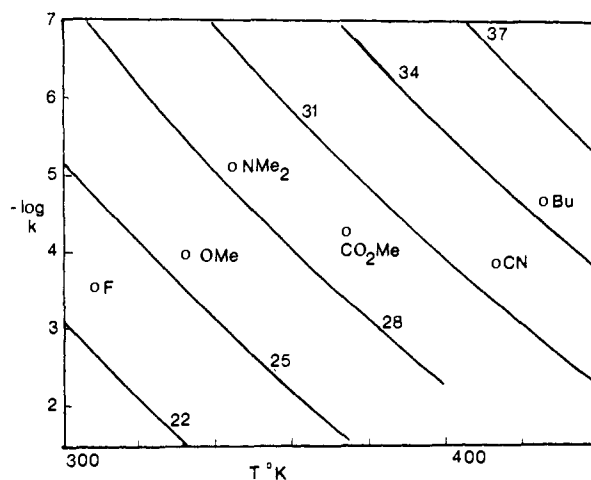


Figure 1. Epimerization of *syn*-bicyclo[6.1.0]nonatrienes. Contour lines are  $\Delta G^\ddagger$  values in kcal/mol.

epimerization *syn*-9-substituted bicyclo[6.1.0]nonatrienes thermolyze with considerably less facility than their anti isomers to distinct products, and therefore the thermolysis of **2b** is most plausibly explained in terms of prior epimerization to **3b**. In contrast the *syn*-fluoro compound **2c** epimerized even at 0°, with  $k_1$  (308°) =  $2.3 \times 10^{-4}$  sec<sup>-1</sup>, to an equilibrium mixture (13:87) with **3c**. **3c** thermolyzed much more readily than other 9-*anti*-bicyclo[6.1.0]nonatrienes, giving a 67:33 mixture of indene (presumed to arise *via* **5c** although monitoring of the reaction by nmr failed to detect an intermediate) and **6c**,  $k_1$  (308°) =  $6.5 \times 10^{-5}$  sec<sup>-1</sup>.

Epimerization has previously been established for *syn*-9-carbomethoxy- and *syn*-9-cyanobicyclo[6.1.0]nonatrienes,<sup>6</sup> although less easily than in the present cases, and lower limits to the barrier for epimerization may be deduced for other substituents. Existing knowledge is summarized in Figure 1. In their previous work, Jones and coworkers considered possible mechanisms for epimerization and concluded that a cleavage of the 1,9 bond followed by rotation and collapse of the resulting biradical was in best accord with their observation. While this cannot be at present formally excluded for our system, the reactivity order F > OMe > NMe<sub>2</sub> > CN is at variance with the expected radical-stabilizing efficiencies of these substituents.<sup>7</sup> While ground-state effects must be important to some extent,<sup>8</sup> alternative mechanisms involving cleavage of the 1,8 bond need to be considered. In this context reversible opening to a ZZZZ or EZZZ cyclononatetraene can be ruled out on account of their

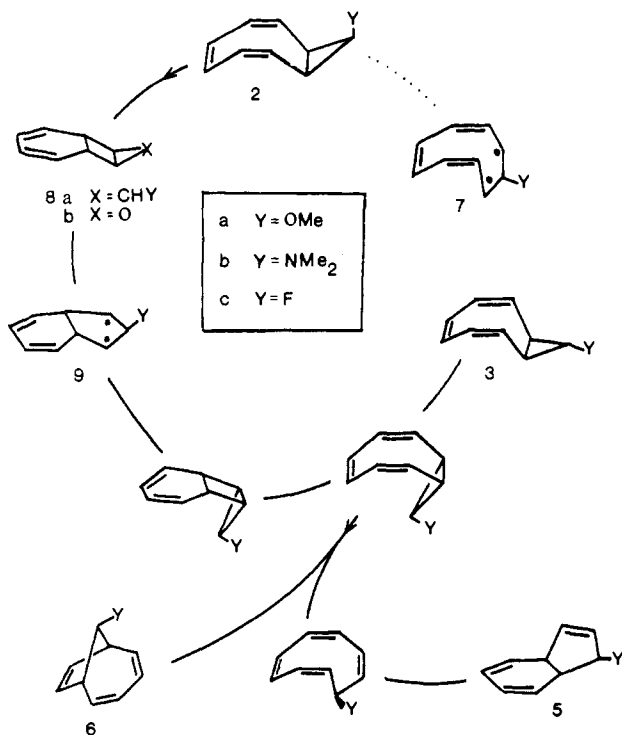
(6) M. B. Sohn, M. Jones, Jr., and B. Fairless, *J. Amer. Chem. Soc.*, **94**, 4774 (1972); A. G. Anastassiou and R. C. Griffith, *Tetrahedron Lett.*, 3067 (1973).

(7) For example, cyclopropylamine thermolyzes much more readily than fluorocyclopropane, and in both cases cleavage of the geminal C-C bond is predominant: K. A. W. Parry and P. J. Robinson, *Int. J. Chem. Kinetics*, **5**, 27 (1973); F. Casas, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3655 (1964).

(8) Cf. J. F. M. Oth, R. Merenyi, H. Rottele and G. Schroeder, *Tetrahedron Lett.*, 3941 (1968); E. Vogel and H.-J. Scholl, private communication to H. Gunther, *ibid.*, 5173 (1970). More significantly nmr evidence suggests that **2c** and **3c** exist entirely in the [6.1.0] form whereas bicyclo[6.1.0]nona-2,6-diene is less stable than bicyclo[5.2.0]nona-2,5-diene. This implies that fluorocyclopropane destabilization is of the same order as the difference in strain energy between cyclobutene and cyclobutane [4 kcal mol<sup>-1</sup>].

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

Scheme I



[4.3.0.0<sup>7,9</sup>]nona-2,4-dienes have been postulated in the room temperature cycloaddition reaction between bicyclo[6.1.0]nonatriene and hexafluorobut-2-yne<sup>11a</sup> and in the thermolysis of *syn*-9-chlorobicyclo[6.1.0]nonatriene.<sup>11b</sup> 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  $\Delta H^\ddagger = 24.8 \text{ kcal mol}^{-1}$  ( $\Delta S^\ddagger = -5 \text{ eu}$ ).<sup>12</sup> 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<sup>13a</sup> and related compounds is substantially faster than that of 5-unsub-

stituted bicyclo[2.1.0]pentanes.<sup>13b</sup> Extended Huckel calculations suggest that epimerization of the corresponding 5,5-difluoro derivative should occur even more readily.<sup>13c</sup> 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 benzenes<sup>14</sup> show that -F and -OMe (but not -NH<sub>2</sub>) 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.<sup>15</sup> 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.<sup>16</sup> 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. Ciganek, *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)

John M. Brown,\* Munro M. Ogilvy

Department of Molecular Sciences, University of Warwick  
Coventry, England

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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.<sup>1</sup> 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-

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(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<sup>-1</sup>; *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[4.3.0.0<sup>7,9</sup>]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).