with liquid N$_2$. Replacement of the liquid N$_2$ by an acetone/dry ice bath afforded removal of the volatile side products. Before sealing the sample tube, NMR solvent was added by distillation: ^{1}H NMR (CD$_2$Cl$_2$, 90 MHz) δ 6.5 (bs, 1 H), 2.8–2.1 (m, 2 H), 2.1–0.9 (m, 9 H); ^{13}C NMR δ 125.8, 101.1, 34.8, 29.4, 28.8, 26.8, 25.4, 15.2; IR (CS$_2$, CCl$_4$) ν 2660, 1768 cm^{-1}. The signal for the cyclopropenyl proton disappeared with the concomitant appearance of another signal at δ 6.4. The second compound, examined by GC/MS, is a dimer: MS *m/e* calcd for C$_{16}$H$_{24}$ 216.1878, found 216.1873; calcd for ^{13}CC$_{15}$H$_{24}$ 217.1912, found 217.1908. Another compound with a parent molecular ion at *m/e* 324 was a trimer of **24**.

Trapping of Bicyclo[5.1.0]oct-1(8)-ene (24) with Butadiene. 1-(Trimethylsilyl)-8-chlorobicyclo[5.1.0]octane (627.7 mg, 2.89 mmol) was allowed to pass through a column of fluoride at 25 °C as described previously. The product **24** was isolated in a cold trap, and butadiene (5 mL) was then distilled onto the cyclopropene. The mixture was then transferred to a 25-mL flask by a double-ended needle, stirred at −30 °C for 2 h, and refluxed for an additional 2 h. Excess butadiene was then removed, and the residue was purified by column chromatography to give 458 mg (96% yield) of tricyclo[5.5.0.0^{1,6}]dec-3-ene (**28**): ^{1}H NMR (300 MHz) δ 6.67 (t, 2 H, *J* = 1.8 Hz), 2.55–2.45 (m, 1 H), 2.45–2.20 (m, 2 H), 2.2–2.08 (m, 1 H), 2.08–1.9 (m, 2 H), 1.9–1.4 (m, 5 H), 1.35–1.08 (m, 3 H), 1.08–0.85 (m, 1 H), 0.8–0.65 (m, 1 H); ^{13}C NMR δ 124.2 (CH), 124.0 (CH), 39.2 (CH$_2$), 32.7 (CH$_2$), 31.4 (CH$_2$), 29.9 (CH$_2$), 28.4 (CH), 26.5 (CH$_2$), 24.8 (CH$_2$), 24.6 (CH), 22.8 (C); MS *m/e* calcd for C$_{12}$H$_{18}$ 162.1409, found 162.1410; calcd for ^{13}CC$_{12}$H$_{18}$ 163.1442, found 163.1438.

Hydrogenation of Bicyclo[5.1.0]oct-1(8)-ene (24). 1-(Trimethylsilyl)-8-chlorobicyclo[5.1.0]octane (771.8 mg, 3.56 mmol) was passed through a fluoride column at 25 °C. The product was collected in a trap that was cooled with liquid N$_2$. Replacement of the liquid N$_2$ by an acetone/dry ice bath afforded removal of the volatile side products. The residue was dissolved in a mixture of pentane (10 mL) and methanol (5 mL) and reduced over 5% Rh/C at 50 psi for 0.5 h. The solution was filtered through silica gel, and the solvents were removed in vacuo. Purification by column chromatography (pentane) gave *cis*-bicyclo[5.1.0]octane (**25**) and methylcycloheptane (**26**). The yields of **25** and **26** were determined to be 53.4% and 28.6%, respectively, by gas chromatography with toluene as an internal standard. The ^{1}H NMR spectrum (300 MHz) of **25** displayed resonances at δ 2.2–2.15 (m, 2 H), 1.85–1.75 (m, 1 H), 1.75–1.6 (m, 2 H), 1.4–1.3 (m, 2 H), 1.2–1.05 (ddt, 1 H), 1.0–0.7 (m, 4 H), 0.7–0.6 (m, 1 H), 0.1–0.0 (m, 1 H); ^{13}C NMR δ 32.7, 31.1, 29.8, 16.4, 14.8. The ^{1}H NMR spectrum (90 MHz) of **26** displayed resonances at δ 0.84 (d, 3 H) and 1.0–1.8 (m, 13 H).

Hydrogenation of *cis*-Bicyclo[5.1.0]octane over Rh/C. A solution of *cis*-bicyclo[5.1.0]octane (389 mg, 3.56 mmol) in pentane (10 mL) and methanol (5 mL) was reduced over 5% Rh/C at 50 psi for 0.5 h. After filtration, the solvents were removed in vacuo and the residue was purified by column chromatography (pentane) to give 370.4 mg of recovered *cis*-bicyclo[5.1.0]octane (95.2%). GC/MS showed no methylcycloheptane.

X-ray Analyses. Colorless crystals of compounds **9** and **10** were mounted at the tips of glass fibers and data were collected as per the parameters listed in Table 1 (supplementary material) with the TEXSAN (v. 2.0, Molecular Structure Corp.) data collection software. Both compounds tended to twin and a number of specimens had to be examined before ones that suitably diffracted were found. The structures were solved with use of the SHELXS86[1] program, which located all of the carbon atoms for both structures. The structures were refined to convergence with the TEXSAN program package.[2] The molecular structures and atom labeling schemes are shown in Figures 1 and 2. Atomic coordinates for the carbon atoms and selected bond metricals are given in Tables 2–5 (supplementary material). The molecules are very similar in the arrangement of the fused-ring system made up of one cyclobutane, two cyclopropane, and two cyclohexane rings. The major difference is that in **9** the cyclohexane rings lie on opposite sides of the cyclobutane moiety while in **10** they occur on the same side. For **9**, the molecule sits about a crystallographic inversion center and only half of the molecule is unique. All C–C bond distances are within the range of normal single bonds. Because of the limited data the carbon atom positions of **10** were only refined isotropically while those of **9** were refined anisotropically. Hydrogen atoms were included in calculated positions that were not refined.

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation for support of this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The National Science Foundation is gratefully acknowledged for support in the purchase of the Rigaku AFC5S diffractometer. We thank Professor George M. Sheldrick for insightful discussions regarding interpretation of the X-ray data. We also thank Professor Kenneth B. Wiberg for providing helpful information on his work with related systems.

Registry No. **1**, 107396-10-1; *trans*-**2**, 135759-60-3; *cis*-**2**, 135663-43-3; **3**, 135663-38-6; **7**, 135663-40-0; **8**, 135695-40-8; **9**, 135720-61-5; **10**, 135663-41-1; **10a**, 135663-39-7; **17**, 58660-83-6; **18**, 90084-82-5; **24**, 135695-42-0; **25**, 286-43-1; **26**, 4126-78-7; **28**, 135663-42-2; tetrabutylammonium fluoride, 429-41-4; 1-bromocyclohexene, 2044-08-8; 1-(trimethylsilyl)cyclohexene, 17874-17-8; 1-(trimethylsilyl)cycloheptene, 61892-24-8; *cis*-1-(trimethylsilyl)-8-chlorobicyclo[5.1.0]octane, 135695-41-9; *trans*-1-(trimethylsilyl)-8-chlorobicyclo[5.1.0]octane, 135759-61-4; 1,3-butadiene, 106-99-0; 1,2-dibromocyclohexane, 5401-62-7.

Supplementary Material Available: Tables of anisotropic displacement parameters for **9** and tables of hydrogen atom positional parameters for **9** and **10** (14 pages); tables of structure factors for **9** and **10** (14 pages). Ordering information is given on any current masthead page.

Is Halogen–Lithium Exchange Intramolecularly Competitive with Removal of an Acidic Hydrogen? Reinvestigation of a Recent Claim

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Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801. *Received May 6, 1991*

Abstract: A careful reinvestigation of a recent report in which the iodine–lithium exchanges of 2-iodo-3-(deuterioxymethyl)quinoline (**1**) and 2-iodo-3-(hydroxymethyl)quinoline (**4**) are interpreted to have occurred prior to abstraction of the alcoholic hydrogen has been carried out. Accurate analyses of the reaction products by FI mass spectrometry give results that are different from those recently reported and are consistent with a mechanism in which removal of the acidic hydrogen takes place prior to iodine–lithium exchange on a molecular scale. The interpretation that suggested the opposite sequence was based on deuterium incorporation values that appear to be inaccurate due to the limitations of the ^{1}H NMR methods used.

In previous work we investigated the lithiations of molecules that contain both an acidic deuterium and an exchangeable bromine or iodine. We suggested that the formation of products in which the deuterium replaces the halogen does not require the interpretation that halogen–lithium exchange is followed by intramolecular deuterium transfer.[1,2] Our results, as well as earlier

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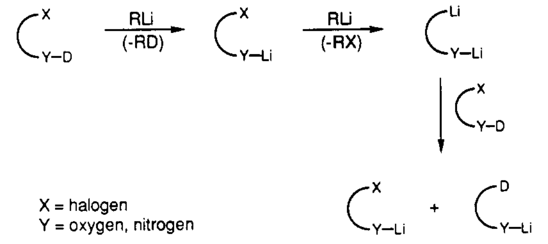
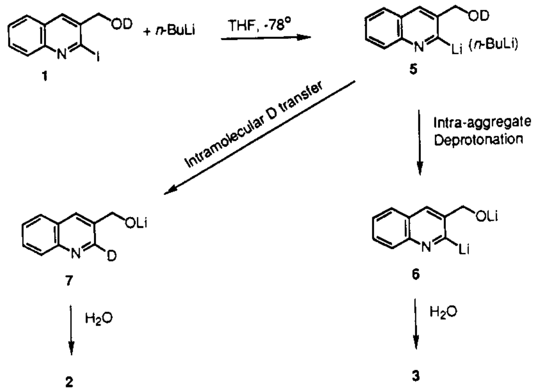
Scheme I

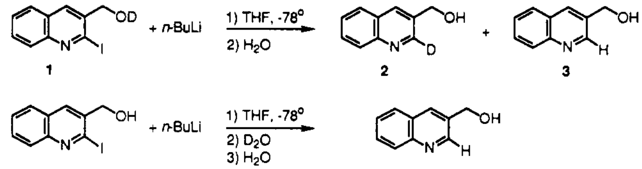


Scheme II



work reported in the literature, were noted to be consistent with an initial deprotonation followed by a halogen–lithium exchange that occurs faster than complete mixing to give a dilithio species. The dilithio species is then subsequently deuterated by unreacted starting material. The general reaction pathway we suggested is shown in Scheme I. This interpretation is supported by the fact that the extent of deuterium transfer was strongly affected by the nature of the mixing of the reactants and limited to no more than 50%.

In a recent paper in this journal, Narasimhan and co-workers reported that treatment of the O-deuterated iodoquinoline **1** with *n*-butyllithium (*n*-BuLi) followed by aqueous workup produced the quinolines **2** and **3** in 90% yield, containing 66% deuterium incorporation based on ^{1}H NMR product analysis corresponding to an absolute yield of 60% of **2**.[3] In addition, these workers reported that treatment of the undeuterated iodoquinoline **4** with *n*-BuLi followed by treatment with D_2O and aqueous workup provided only **3** containing no deuterium.



Narasimhan and co-workers pointed out that their results were inconsistent with the mechanism of Scheme I, which would limit the yield of **2** to a maximum of 50%. They proposed a mechanism, summarized in Scheme II, in which iodine–lithium exchange occurs prior to removal of deuterium to form complex **5** and is followed by the intramolecular transform of deuterium. The presence of 66% of the deuterated product **2** (rather than 100%) was attributed to some intraaggregate deprotonation taking place by *n*-BuLi in complex **5** to form the dilithiated species **6**. The conversion of **4** to **3** presumably occurs by a similar pathway, although the total absence of **2** could not be explained.

We reinvestigated the lithiations of **1** and **4**, initially to establish whether there were special features of this structure that might obviate the mechanism of Scheme I. However, we have found that mass spectrometric analyses of the products indicated deuterium incorporations in the products that are quite different from those previously reported. In this paper we report the details of our reinvestigation of the lithiations of **1** and **4** and our interpretation that iodine–lithium exchange in **1** and **4** is not faster than removal of the respective acidic hydrogens in an intramolecular competition. We believe Narasimhan and co-workers' recent suggestions of the opposite sequence of reactivity have been based on inaccurate ^{1}H NMR product analyses.[3]

Table I. Percentage of **2** in the Mixture of **2** and **3** from the Reactions of **1** or **4** with *n*-BuLi

reactant	molarity[a]	quench	% **2**[b]	% yield[c]
1	0.1	CH_3OH	29	72
1	0.05	CH_3OH	32	69
1	0.05	CH_3OH	27	67
4	0.1	CH_3OD	65	73
4	0.05	CH_3OD	68	73
4	0.05	CH_3OD	60	76

[a] Concentration of solution of **1** or **4** in THF prior to addition of *n*-BuLi. [b] Deuterium incorporation for the quinoline product mixture of **2** and **3** as determined by FIMS analysis (±5%). [c] Isolated yield of quinoline product after HPLC purification.

Table II. Percent of **2** in the Known Mixtures of **2** and **3** As Evaluated by FIMS and ^{1}H NMR

authentic mixture[a]	FIMS value[b]	^{1}H NMR values[c]
50%	50%	68% (58%)
43%	47%	64% (57%)

[a] Value expected from the ratio of deuterated and undeuterated standards in mixture. [b] Value obtained by FIMS isotope ratio determination. [c] Values obtained by integration of ^{1}H NMR spectra with use of default instrument parameters. Values in parentheses were obtained by integration of spectra with extended delay times.

Results and Discussion

The nondeuterated iodoquinoline **4** synthesized in 70% yield from the known aldehyde provided spectral data consistent with that reported previously and met common criteria for purity, including elemental analysis.[3,4] The O-deuterated iodoquinoline **1** was produced by treatment of **4** with methanol-*d* in THF followed by removal of the solvents in vacuo. Two such cycles were carried out followed by at least 36 h under high vacuum to ensure complete removal of solvent.

We carried out a number of reactions of **1** or **4** with 2 equiv of *n*-BuLi. A stock solution of *n*-BuLi was added to a solution of **1** or **4** in THF at −78 °C, and the reaction was stirred for 10 min followed by quenching with either CH_3OH, when starting with **1**, or CH_3OD, when starting from **4**. The reactions were allowed to warm to room temperature and then purified to obtain the quinoline product as a mixture of **2** and **3**, which was analyzed for deuterium content by field ionization mass spectrometry (FIMS). The mixtures of **2** and **3** were isolated in 67–76% yields. Our results are summarized in Table I.

As is evident in the table, these results differ significantly from those recently reported.[5] When starting with deuterated **1**, we found considerably less deuterium incorporation in our products, including 0.1 M reaction, which previously was reported to give 66% d_1 product.[3] A discrepancy between our results and those of Narasimhan and co-workers is also found when starting with nondeuterated **4** and quenching with CH_3OD. As can be seen

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(1) Beak, P.; Chen, C. W. *Tetrahedron Lett.* **1985**, *26*, 4979.

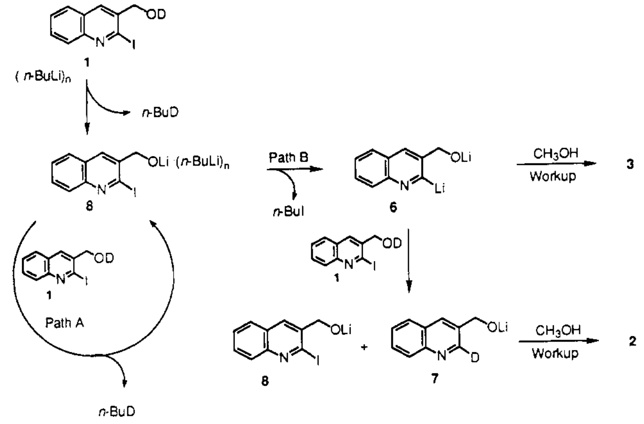
(2) Beak, P.; Musick, T. J.; Chen, C. W. *J. Am. Chem. Soc.* **1988**, *110*, 3538.

(3) Narasimhan, N. S.; Sunder, N. M.; Ammanamanchi, R.; Bonde, B. D. *J. Am. Chem. Soc.* **1990**, *112*, 4431.

(4) Meth-Cohn, O.; Narine, B.; Tarnowski, B.; Hayes, R.; Keyzad, A.; Rhouati, S.; Robinson, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2509.

(5) We used a solution of *n*-BuLi in hexanes for these reactions and note that Narasimhan and co-workers used an *n*-BuLi solution in Et_2O. In order to establish whether the change in solvent could have caused the differences in the observed results, we also carried out reactions using a solution of *n*-BuLi in Et_2O. No substantial changes in our results were found. It should also be noted that while Narasimhan and co-workers reported their results as the absolute yields of the deuterated products, we have reported our results in terms of the deuterium incorporation of the products. In order to obtain pure products, we used reverse-phase HPLC methods, which invariably resulted in some loss of product. Thus, we consider the deuterium incorporation values to be a better indicator of the results for these reactions.

Scheme III



in Table I, we found substantial deuterium, incorporation in all cases. Narasimhan and co-workers report no deuterium incorporation for this reaction when deuterium oxide was used as the quenching reagent.[6] We attribute the minor differences in the values observed in Table I to the unavoidable differences in mixing efficiency between nominally identical reactions. Other reactions in which stirring was not necessarily kept constant (e.g., by use of different size stirring bars or rates of stirring) gave results that tended to vary more, but were in the range of 20–40% d_1 when starting from **1**. A strong dependence on mixing efficiency for these types of reactions has been noted.[2]

We have verified that the isotope ratio values are correct by preparation and evaluation of known standard mixtures. Treatment of **1** with *n*-BuLi followed by quenching the methanol-*d* and purification provided essentially pure **2** (>95% d_1) as determined by FIMS. Known mixtures of **2** and **3** were then prepared and submitted for FIMS analysis. The results, shown in Table II, indicate that the isotope ratio values provided by FIMS are correct within an experimental error of ±5%.

On the other hand, our ^{1}H NMR analysis of the authentic mixtures of **2** and **3** provided inaccurate deuterium incorporations. Using standard instrumental parameters and comparing the area of the signals of the benzylic and C_2H protons gave values for the percentage of **2** that were high by 30–40% (i.e., 15% at the 50% level). Since Narasimhan and co-workers used a similar ^{1}H NMR analysis and based their claim of >50% deuterium incorporation on this method, we believe they were misled as to the amount of **2** present. Sources of error leading to inaccurate integrations are known, and there are a number of parameters that must be chosen carefully.[7] Indeed, even when we used extended delay times to accommodate the different relaxation times of the protons compared, a somewhat high percentage of **2** was obtained from the mixture of **2** and **3**.[8] We strongly suggest the use of FIMS for the determination of isotope ratios in which the knowledge of isotopic incorporation is crucial.[9] If ^{1}H NMR integrations are used to determine deuterium incorporation, careful choice of parameters is needed as well as verification of the method by the use of known standard mixtures.

On the basis of the results of this study, we propose the mechanism shown in Scheme III, in which removal of the acidic deuterium occurs prior to iodine–lithium exchange. Upon treatment with *n*-BuLi, deprotonation of **1** occurs to give the alkoxide complex **8** and deuterated butane. The alkoxide **8** can then react with additional **1**, producing another molecule of butane-d_1 and additional alkoxide (path A). However, competing with path A is a halogen–lithium exchange (path B) that produces the dianion **6**, which can also react with **1** to provide the deuterated alkoxide **7**, which on workup leads to **2**. If the starting material **1** is consumed by either path A or by the reaction with **6** to provide the alkoxide **7**, any remaining *n*-BuLi converts the alkoxide **8** into the dianion **6**. Since **1** has been consumed, this dianion remains until workup, which provides the nondeuterated product **3**. A similar analysis applies to the reaction of **4** with *n*-BuLi followed by CH_3OD quenching. The extents of deuteration from **1** and from **4** are obversely related as expected from this scheme. If path A alone was operative in the reaction of **1** with 2 equiv of *n*-BuLi, only **3** would be formed. If only path B was followed, 50% **2** would be expected. While quantitative interpretation of the results in Table I is not warranted due to the unknown effects of *n*-BuI produced in situ, irregularities in mixing, and the possible differences in reactivity of different aggregates, the results are consistent with the competitive pathways depicted in Scheme III.

This present work and the results presented earlier[1,2] are consistent with deprotonation occurring prior to halogen–lithium exchange on a molecular scale. It is important to note that, this means for each individual molecule of iodoquinoline, deprotonation occurs first. In the bulk solution, however, there is alkoxide undergoing iodine–lithium exchange prior to deprotonation of remotely located iodoquinoline **1** due to the noninstantaneous mixing. It is this process that leads to the in situ transfer of a hydrogen or deuterium, which gives the appearance of halogen–lithium exchange being faster than deprotonation. Although we believe that no convincing evidence has yet been presented that halogen–lithium exchange occurs faster intramolecularly than removal of an acidic hydrogen, we do not wish to imply that there can be no process faster than deprotonation.[10]

In summary, our reinvestigation of the reactions of the iodoquinolines **1** and **4** with *n*-BuLi gives results and requires interpretations that are different from those most recently suggested for these reactions.[3] Accurate product analyses are consistent with removal of the acidic hydrogen prior to iodine–lithium exchange on a molecular scale, a result that is consistent with our previous reports.[1,2] We suggest that the procedures used in this work and those described previously be applied to related reactions in which the relative order or rates of a formal intramolecular competition need to be established.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 or 300 MHz with tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported relative to TMS or residual chloroform for ^{1}H spectra and $CDCl_3$ for ^{13}C spectra. Preparative HPLC was performed on a Dynamax 21.4-mm preparative C_{18} column. Melting points were determined on a Buchi melting point apparatus and are uncorrected. Microanalyses were obtained from the University of Illinois Microanalytical Service Laboratory. Field ionization mass spectra (FIMS) were obtained at the University of Illinois School of Chemical Sciences Mass Spectrometry Facility. Isotope incorporation values were calculated by using standard matrix methods.

Tetrahydrofuran (THF) was distilled from sodium/benzophenone. The solution of *n*-butyllithium in hexanes (*n*-BuLi) was purchased from

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(6) The observation of Narasimhan and co-workers that no deuterium incorporation is found on treatment of **4** with *n*-BuLi followed by D_2O quenching seems inconsistent with our experiments, which show fairly high deuterium incorporation using methanol-*d*. A possible explanation is that at the low temperature of quenching (−78 °C) D_2O is not an effective trap and substantial amounts of the unquenched material may remain until water workup. Difficulties with D_2O as a low-temperature trap have been reported previously.[12] In fact, if the reaction starting with **1** and quenching with H_2O workup were to proceed as shown in Scheme II to give 66% **2**, then the sequence starting with nondeuterated **4** followed by quenching with D_2O should give ~33% **2**. However, it was reported that when starting with **4**, no **2** (0% deuterium incorporation) was detected.[3]

(7) Derome, A. E. *NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, 1987; pp 168–172.

(8) The two benzylic protons (4.8 ppm) were shown to have a T_1 value of 2.0 s, while the C_2H proton (8.8 ppm) has a T_1 value of 3.5 s. Since these values are quite different, insufficient delay times would decrease the intensity of the signal at 8.8 ppm, thus falsely indicating a higher deuterium incorporation than was actually present. The NMR integration values obtained with extended delay times were still elevated, although they were in the range of 10–15% error.[7] Narasimhan and co-workers do not report the use of any special parameters for their NMR integrations.[3]

(9) FIMS has been used in our laboratories extensively due to its "softer" ionization, which produces larger M^+ ions than EIMS. In addition, FIMS usually produces smaller M − 1 peaks, which can interfere with the isotope ratio determinations.

(10) The carefully executed studies of Okamura and co-workers on vinyl sulfoxides are especially interesting. Park, G.; Okamura, W. H. *Synth. Commun.*, in press. Theobold, P. G.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 741. Theobold, P. G.; Okamura, W. H. *Tetrahedron Lett.* **1987**, 6565.

J. Am. Chem. Soc. **1991**, *113*, 7987–7994

Lithium Corp. and was titered prior to use by the method of Suffert.[11] The 2-iodo-3-formylquinoline was prepared according to literature procedures[4] and was recrystallized from ethanol prior to use. All other reagents were obtained from commercial sources and used without purification unless otherwise noted. Reactions were carried out with standard Schlenk glassware and techniques.

Preparation of 2-Iodo-3-(hydroxymethyl)quinoline (4). To a solution of 2-iodo-3-formylquinoline (2.10 g, 7.40 mmol) and 1 drop of 20% NaOH solution in 150 mL of methanol cooled to 0 °C was added 0.15 g of NaBH$_4$ in small portions. The reaction was then stirred at 0 °C for 15 min, during which time a precipitate formed. The reaction was poured onto ice and filtered to yield a tan solid, which was recrystallized from ethanol to yield 1.68 g (5.88 mmol, 79%) of **4** as a light tan solid, mp 183–184 °C. The material gave ^{1}H and ^{13}C NMR spectra consistent with those reported previously.[3] Anal. Calcd for C$_{10}$H$_8$INO: C, 42.13; H, 2.83; N, 4.91; I, 44.51. Found: C, 42.40; H, 2.83; N, 4.92; I, 44.21.

Representative Preparation and Reaction of 2-Iodo-3-(deuteriooxymethyl)quinoline (1) with *n*-BuLi, Followed by CH$_3$OH Quenching. A solution of **4** (0.1377 g, 0.483 mmol) in 5 mL of dry THF and 5 mL of CH$_3$OD was stirred for 8 h, and then the solvents were removed in vacuo. Additional THF and CH$_3$OD (5 mL each) were added, and the reaction was stirred for 10 h followed by removal of the solvents in vacuo. The sample was kept under high vacuum for 48 h, and then 9.5 mL of dry THF was added and the solution cooled to −78 °C. *n*-BuLi (0.97 mmol, 1.4 M, 0.69 mL) was added dropwise, and the reaction was stirred at −78 °C for 10 min and then quenched by addition of CH$_3$OH (0.8 mL). The reaction was warmed to room temperature, poured into NH$_4$Cl solution, and extracted three times with Et$_2$O. The combined organic layers were dried over MgSO$_4$, filtered, and the solvents removed in vacuo. Purification by reverse-phase HPLC (50% CH$_3$OH/H$_2$O) provided 0.0533 g (0.335 mmol, 69%) of a mixture of the deuterated and undeuterated 3-(hydroxymethyl)quinolines **2** and **3** as a white solid, mp 82–83 °C. FIMS analysis of the product relative to an undeuterated standard indicated a deuterium content of 32%.

Representative Reaction of 2-Iodo-3-(hydroxymethyl)quinoline (4) with *n*-BuLi, Followed by CH$_3$OD Quenching. To a solution of **4** (0.1547 g, 0.543 mmol) in 11 mL of dry THF cooled to −78 °C under N$_2$ was added *n*-BuLi (1.1 mmol, 1.4 M, 0.78 mL) dropwise. The reaction was stirred at −78 °C for 15 min, and then 0.8 mL of CH$_3$OD was added. The reaction was stirred at −78 °C for 15 min and then warmed to room temperature and poured into a saturated NH$_4$Cl solution. The mixture was extracted with Et$_2$O three times, the combined organic layers were dried over MgSO$_4$ and filtered, and the solvent was removed in vacuo. Purification by reverse-phase HPLC (50% CH$_3$OH/H$_2$O) provided 0.0652 g (0.408 mmol, 76%) of **2** and **3** as a white solid, mp 81–82 °C. FIMS analysis indicated a deuterium incorporation of 60%.

Preparation of 2-Deuterio-3-(hydroxymethyl)quinoline (2) for Use as a Deuterated Standard. Starting from 0.2258 g (0.792 mmol) of **4**, the O-deuterated quinoline **1** was prepared as described above and then dissolved in 15 mL of dry THF. To this solution was added *n*-BuLi (1.65 mmol, 1.5 M, 1.1 mL) dropwise. The reaction was stirred for 15 min and then quenched by addition of 1.0 mL of CH$_3$OD. The reaction was stirred for 15 min at −78 °C and warmed to room temperature. The reaction mixture was poured into saturated NH$_4$Cl and extracted three times with Et$_2$O. The combined extracts were dried over MgSO$_4$ and filtered, and the solvent was removed in vacuo. Purification by HPLC (50% CH$_3$OH/H$_2$O) provided 0.896 g (0.560 mmol, 71%) of **2** as a white solid: mp 80–82 °C; ^{1}H NMR (CDCl$_3$) δ 4.39 (b, 1 H), 4.83 (s, 2 H), 7.48 (t, 1 H), 7.62 (t, 1 H), 8.00 (d, 1 H), 8.06 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 62.27, 126.78, 127.67, 127.83, 128.54, 129.31, 133.85, 133.92, 146.97, 149.52 (t, $J_{\text{C-D}}$ = 27.1 Hz). FIMS analysis relative to a undeuterated standard indicated a deuterium incorporation of >95%.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this work and to Professor William Okamura for discussion and a preprint.

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[11] Suffert, J. *J. Org. Chem.* **1989**, *54*, 509.

[12] Bailey, W. F.; Patricia, J. J.; Nurmi, T. T.; Wang, W. *Tetrahedron Lett.* **1986**, 1861.

Is the McConnell Mechanism a Suitable Strategy for the Design of Molecular Ferromagnets?

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Abstract: We present a qualitative discussion of a mechanism ascribed to McConnell that is supposed to predict ferromagnetic behavior for certain orbital configurations of the molecules in a stack of alternating donor and acceptor units. We examine in detail the possible mixing of ground and charge-transfer configurations of a donor–acceptor pair for both singlet and triplet states. It is shown that more charge-transfer mixing terms are available for the stabilization of the singlet as compared to the triplet. In contrast to McConnell's assumption, this will result in a singlet ground state if the Hubbard-like charge-transfer parameter Δ is much larger than the singlet–triplet splitting of the charge-transfer configurations governed by an exchange integral, *K*. In addition, a modification of McConnell's mechanism for uniform stacks is discussed. In this case, a triplet ground state of the dimer might be obtained only for a highly symmetrical arrangement of the molecules in the stack.

1. Introduction

Molecular ferromagnets have been a challenge to both experimentalists and theorists for some time. Different strategies have evolved for the design of these materials.

On the basis of the existence of high-spin organic molecules, some models for purely organic ferromagnetic polymers with a conjugated π system have been suggested.[1] The ferromagnetic behavior of these hypothetical compounds is a consequence of the topology of their π electron network, which gives rise to degenerate nonbonding orbitals in accordance with the Coulson–Rushbrooke theorem.[2] Hund's rule then suggests a parallel alignment of the spins of the radical electrons in these singly occupied orbitals. Although tetracarbene and pentacarbene molecules with nonet and decet ground states, respectively, could be synthesized,[3] no real polymeric material of this kind is known as yet. A related concept also based on the topology of conjugated polymers suggests a ferromagnetic coupling of polarons.[4]

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[1] (a) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372. (b) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. (c) Tyutyulkov, N.; Schuster, P.; Polansky, O. E. *Theor. Chim. Acta* **1983**, *63*, 291. (d) Tyutyulkov, N.; Polansky, O. E.; Schuster, P.; Karabunarliev, S.; Ivanov, C. I. *Theor. Chim. Acta* **1985**, *67*, 211.

[2] Coulson, C. A.; Rushbrooke, G. S. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 193.

[3] (a) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. (b) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147. (c) Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1990**, *112*, 4074.

[4] Fukutome, H.; Takahashi, A.; Ozaki, M. *Chem. Phys. Lett.* **1987**, *133*, 34.

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