Reaction of Cycyohexylammonium Chloride with (+)-Phenylneopentylmethylbromosilane. Treatment of (+)-phenylneopentylmethylbromosilane (1.71 g), $[\alpha]_D$ +3.8° (*c* 11.4 in CCl_4), with cyclohexylammonium chloride (0.85 g) in chloroform (60 ml) gave (−)-phenylneopentylmethylchlorosilane (1.17 g) in 82% yield with $[\alpha]_D$ −1.6° (*c* 5.9 in CCl_4) and having the expected infrared spectrum.

Reaction of Lithium Dimethoxyaluminum Hydride with (+)-Phenylneopentylmethylchlorosilane. Reaction of (+)-phenylneopentylmethylchlorosilane (1.18 g), $[\alpha]_D$ +7.5° (*c* 11.8 in CCl_4), with excess lithium dimethoxyaluminum hydride (prepared from the hydride and methanol)[4g] for 2 hr gave 1.07 g of product shown to be ~55% methoxysilane and 45% silane by an infrared spectrum. The rotation of the mixture was $[\alpha]_D$ −4.9° (*c* in 10.7 in pentane). The mixture was placed on a column of silica gel and allowed to stand for 12 hr. Elution with pentane-benzene (50%) gave (−)-phenylneopentylmethylsilane (0.49 g) in 49% yield with $[\alpha]_D$ −2.3° (*c* 4.9 in CCl_4). Therefore, by difference, the (−)-methoxysilane (0.58 g) had $[\alpha]_D$ −8.2° (*c* 5.8 in pentane).

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Stereochemistry of Electrophilic Substitutions on 2-Norbornyllithium

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Abstract: It has been demonstrated that brominolysis of *exo*- and *endo*-2-norbornyllithium occurs with predominant inversion of configuration, while carboalkoxylation (with chloroformate esters) occurs with preferred (but not complete) retention. It is concluded that concerted aliphatic electrophilic substitutions, in contrast with nucleophilic substitutions, have both inversion and retention pathways available, and the pathway chosen depends upon subtle factors not yet elucidated.

The stereochemistry of concerted electrophilic aliphatic substitutions has been studied by a number of workers in the past two decades, and the result has been a considerable body of data to indicate that such substitutions prefer retention of configuration. Examples are the carbonations of secondary alkyllithiums,[1,2] alkenyllithiums,[2,3] and cyclopropyllithiums;[4,5] the halogen–metal interchanges in the same systems;[1,3–5] metal–metal exchanges of saturated[2,6,7] and olefinic[2] organomercurials; and brominolysis of cyclohexylmercuric bromides[8] and cyclopropyllithiums.[4] In the last-named case, Applequist and Peterson found that *cis*- and *trans*-2-methylcyclopropyllithium reacted with bromine with preferential but incomplete retention of configuration. The experiments herein described were conceived to explore the reason for this incomplete retention.

Absence of stereospecificity in a substitution reaction first suggests an intermediate carbanion, radical, or cation. Arguments against the carbanion had been raised[4] in the cyclopropyl case, where the lithium reagents show no tendency to epimerize at the lithiated carbon, so the most probable possibilities seemed to be the free radical, which had already been found[8] in organomercurial brominolyses under certain conditions, and the carbonium ion, which might react under some conditions with a nucleophile before it can open to the allylic cation. The radical and cation possibilities, it was thought, could be differentiated in the 2-norbornyl case, which should give considerable *endo*-norbornyl bromide in any reaction of norbornyl radical with bromine,[9] but exclusively *exo* product from the norbornyl cation with bromide.[10] Furthermore, from an optically active norbornyllithium, only the cation mechanism should lead to racemized product.[10–12] Because of the unexpected results obtained in this work with the racemic norbornyllithiums, it proved unnecessary to examine the optically active forms.

Results and Discussion

2-Norbornyllithium was prepared from *exo*-2-norbornyl chloride and lithium metal in refluxing pentane in yields as high as 33%, but averaging about 10%. *endo*-2-Norbornyl chloride also gave yields of about 10%. The same *exo*/*endo* mixture of lithium reagents was formed in either case, as shown by the near identities of the product ratios from reactions with various electrophiles at −70° (Table I). Also to be noted in Table I (footnotes) is that several efforts to change the composition of the cold epimeric lithium reagent mixture by selective destruction of the more reactive epimer failed to change the final product mixtures significantly. Finally, and most importantly, the data show that the different reagents give very different product mixtures, which means that at least some of the reactions do not proceed with simple retention of configuration.

Suitable controls, described in the Experimental Section, were done to establish the stabilities of all

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Table I. Reaction Products at −70° from Norbornyllithium Prepared in Refluxing Pentane

Reagents	Starting chloride	Product[a]	Product ratio,[b] *endo/exo*	No. of runs	Av. yield, %
$ClCO_2CH_3$	*exo*	RCO_2CH_3	0.383 ± 0.028[c]	8	29.4
	endo		0.413 ± 0.020[d]	4	35.8
(1) CO_2; (2) HCl; (3) BF_3, CH_3OH	*exo*	RCO_2CH_3	0.198 ± 0.052[e]	6	51.1
	endo		0.195 ± 0.02[f]	3	69.0
Br_2	*exo*	RBr	1.683 ± 0.254	4	75.8
	endo		1.543 ± 0.178[g]	5	35.9
$BrCH_2CH_2Br$	*endo*	RBr	0.233 ± 0.004	1	41

[a] R = 2-norbornyl. [b] Errors are average deviations for the several runs, except where there was only one run, and then it is an average deviation of several measurements of the ratio. [c] Includes a run (0.430) in which there was inverse addition of lithium reagent to methyl chloroformate; a run (0.399) in which half of the lithium reagent was destroyed with 2,4,6-triisopropylbenzophenone prior to the reaction; and two runs (0.391 and 0.300) in which part of the lithium reagent was allowed to react with bromine prior to addition of chloroformate. [d] Includes a run (0.453) in which part of the lithium reagent was allowed to react with bromine prior to addition of chloroformate and a run (0.401) in which part of the lithium reagent was allowed to react with allyl bromide prior to successive reactions with bromine and methyl chloroformate. [e] Includes a run (0.211) in which half of the lithium reagent was decomposed with 2,3,6-triisopropylbenzophenone prior to carbonation. [f] Includes a run (0.226) in which the lithium reagent was partially destroyed with allyl bromide prior to carbonation. [g] Includes a run (1.335) in which the lithium reagent had been partially destroyed with allyl bromide and a run (1.365) in which it had been partially destroyed with benzophenone.

of the products under the reaction and isolation conditions.

Whether the nonretention processes involve free radical or other trivalent intermediates seems best determined by finding the product ratios formed from the individual epimeric lithium reagents. Ideally, the pure *exo*- and *endo*-lithium compounds should be prepared, but the products from each epimer can also be determined from two mixtures of lithium reagents of known compositions, albeit with some loss of precision.

It was found that the epimeric chlorides could occasionally be made to react with lithium at 20° in pentane to give low yields (1–4%) of lithium reagents, which were cooled to −70° and treated with the same reagents as above to give the products shown in Table II. Because of the low yields of lithium reagent, not every reagent could be tried on every organolithium mixture, but the data obtained show clearly that different mixtures of lithium reagents were obtained from the two chlorides, and that the mixture obtained in refluxing pentane has an intermediate composition. Reproducibility from one run to another is not to be expected, since different degrees of epimerization might occur prior to cooling, but the product ratios from any one run should all represent the ratios from just one lithium reagent mixture.

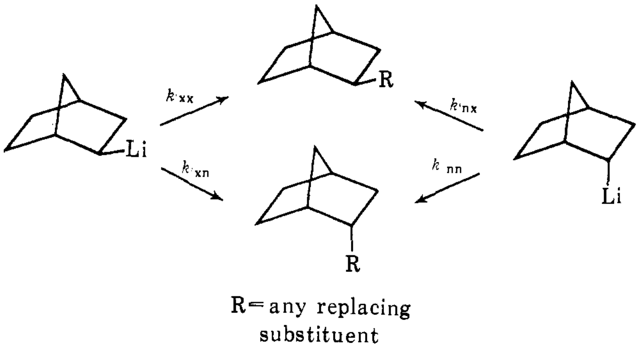
Table II. Reaction Products at −70° from Norbornyllithium Prepared in Pentane at 20°

Run no.	Starting chloride	Reagent	Product ratio,[a] *endo/exo*
1	*exo*	$ClCO_2CH_3$	0.293 ± 0.014
		CO_2[b]	0.089 ± 0.006
		Br_2	2.44 ± 0.06
2	*exo*	$ClCO_2CH_3$	0.272 ± 0.006
		Br_2	3.04 ± 0.08
3	*endo*	Br_2	0.644 ± 0.09

[a] The errors are average deviations of several analyses of the product of each reaction. [b] Carbonation was followed by formation of the methyl esters for analysis, as in Table I.

The data of Table I and of run 1 in Table II now permit a calculation of some of the rate constant ratios for the epimeric organolithiums. Reference to Scheme I should be made for definitions of the rate constants. The similar stereospecificities for the carbonation and ethylene dibromide reactions (Table I), the obviously high stereospecificity of carbonation (Table II, run 1), and the previously known high stereospecificities with carbon dioxide make it reasonable to assume that carbonation is 100% stereospecific with retention, and this assumption provides the best approach to a determination of the *endo/exo* ratio of the lithium reagent. (The low yields of lithium reagents and the high yields of contaminating by-products made nuclear magnetic resonance analysis impractical.) The ratio for the reagents prepared in refluxing pentane is, therefore, taken to be 0.197 (from Table I), and the ratio for the mixture prepared in run 1 of Table II is 0.089. If it is assumed that *exo*- and *endo*-norbornyllithium are consumed with the same rate constant (as would be the case if the reactions are diffusion controlled), then eq 1 is obeyed, where r is the *exo/endo* ratio of products, b is the *endo/exo* ratio of lithium reagents, f is $k_{xx}/(k_{xx} + k_{xn})$, and g is $k_{nx}/(k_{nx} + k_{nn})$. Support for the assumption of equal reactivities of the two epimeric lithium reagents is found in several experiments in which the lithium reagent was only partially allowed to react or was partially destroyed before the reaction of interest (Table I). No effect on the product ratio was observed in any of these cases.

Scheme I



$$r = (f + bg)/[(1 - f) + b(1 - g)] \qquad (1)$$

The values of the rate constant ratios obtained by simultaneous solution of pairs of equations of type 1 for the data of Table I and Table II, run 1, are shown in Table III.

One interesting fact made apparent by the foregoing treatment of the data is that for $ClCO_2CH_3$, the preference for retention is about the same in the *exo*-lithium reagent as in the *endo*-; *i.e.*, $(k_{xx}/k_{xn})(k_{nx}/k_{nn}) \simeq 1$. Although one cannot now define the factors which favor retention or inversion mechanisms, it is clear that the factors are not very different in these two epimers, and hence that there is no large steric obstacle to *endo* attack at the 2-norbornyl position. This fact

Table III. Rate Constant Ratios for Reactions of *exo*- and *endo*-Norbornyllithium[a]

Reagent	k_{xx}/k_{xn}	k_{nx}/k_{nn}
$ClCO_2CH_3$	4.82 (4.30 to 5.02)	0.188 (0.070 to 0.316)
Br_2	0.248 (0.241 to 0.349)	. . . (−9.5 to 5.3)[b]

[a] Values in parentheses represent the extreme values calculated from the data by adding or subtracting the average deviations. [b] No meaningful value can be obtained because of the insensitivity of r to the ratio k_{nx}/k_{nn}. The calculated value from the average data is −4.09.

is in accord with stereochemical patterns observed in reactions of the norbornyl free radical,[9] and gives scant support to the view that the preferential attack of nucleophiles on the *exo* side of the supposedly unbridged norbornyl cation is due to a steric hindrance to *endo* attack.[13]

It is quite clear from the above analysis that *exo*-norbornyllithium reacts with bromine with preferential inversion, and from the fragmentary information on the *endo*-lithium compound, especially Table II, run 3, it seems probable that the latter also reacts with preferential inversion. As far as the present authors are aware, there is no previous example in which a concerted electrophilic, intermolecular substitution on an aliphatic or alicyclic system has been shown to go with preferred inversion. The *availability* of inversion pathways in such substitutions has been previously evident,[14,15] but only in circumstances where the substitution with retention was precluded or led to no net reaction.

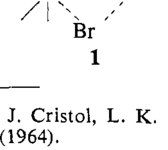
The variable stereochemistry of the reactions reported here is highly reminiscent of the situation found in reactions involving base-generated carbanions from hydrocarbon, ketone, alcohol, sulfone, and other functional groups.[16] Indeed, it is not possible to exclude the possibility that the reactions of the organolithiums proceed through carbanions and that the stereochemistry is controlled by ion pair and solvent association effects of the types proposed by Cram in the familiar carbanion systems.[16] Arguments against such carbanion intermediacy in the reactions reported here can be made, however. First, the possibility that the lithium reagents spontaneously dissociate to carbanions prior to reaction with the electrophiles, and that the reacting carbanions thus formed do not retain their original stereochemistry, could account for some loss of stereospecificity, and might even be consistent with a net inversion of stereochemistry. Such a possibility is inconsistent with the fact that net inversions and nonstereospecific retentions occur under conditions where the lithium reagents do not epimerize, both in the present work and in the cyclopropyl system.[4]

A second and more serious possibility is that the electrophilic agents *induce* the dissociation of the alkyllithiums to ion pairs. Against this possibility is the weak lithiophilic character which might be expected for such reagents as bromine or methyl chloroformate, and also the difficulty of formulating a spatial arrangement of organolithium and bromine that would be expected to lead to predominant inversion. These arguments are certainly not conclusive.

The question of the possible intermediacy of free radicals in any of the reactions reported here cannot be resolved completely. In the case of the chloroformate reactions, the observed stereochemical behavior (see especially Table III) certainly rules out major contributions of the free norbornyl radical, which would be expected to lead to $k_{xx}/k_{xn} = k_{nx}/k_{nn}$, assuming that it could give the observed ester product at all. The case of brominolysis is not so clear but it is known in a number of circumstances[9,17] that norbornyl and substituted norbornyl radicals react with bromine to form the bromides in an *exo*/*endo* ratio of 70/30. The preferred formation of *endo* bromide from *exo*-lithium reagent is by itself nearly incompatible with a major free-radical pathway, and the apparent preferred formation of *exo* bromide from *endo*-lithium reagent (Table II, run 3) supports this conclusion. The possibility that there are free radicals but that stereochemistry is controlled by cage effects could account for a preferred retention, as observed in chloroformate reactions, but would not conveniently explain preferred inversion.

It is not clear now whether the results obtained on the norbornyl system can be extrapolated to predict stereochemistry of the same reactions in simple alkyl systems. Such systems must be investigated next, and, in fact, would have been investigated first except for the free-radical and cation hypotheses which arose from the stereochemical work on the 2-methylcyclopropyl system.[4] The surprising outcome of the present experiments suggests that the concerted inversion and retention pathways for concerted electrophilic aliphatic substitution are inherently about equally available, and that changes in reagents and perhaps solvents[4] tip the scales in favor of one or the other. Far more data are needed to see exactly what the controlling factors are.

Matteson and co-workers[18,19] have shown that while the mercuri-deboronation reaction exhibits the usual retention of configuration, the reactions of the norbornene-5-boronic acids and bicyclo[2.2.2]octene-5-boronic acids proceed with attack on the double bond and transannular displacement of boron, and these reactions show a strong preference for inversion of configuration at the 5-carbon. They have considered the general problem of electrophilic substitution stereochemistry and have suggested an important role for cyclic transition states in those cases where retention is favored. In these terms, perhaps ethylene dibromide reacts with a lithium reagent by retention because of a favorable six-membered cyclic transition state (**1**)



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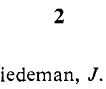

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while bromine avoids the less favorable four-membered ring (**2**). Carbon dioxide and methyl chloroformate may have great enough affinities for lithium to go by four-membered transition states in spite of some inherent preference for inversion. These thoughts are speculations rather than conclusions at this point, but offer many suggestions for future experiments.

Experimental Section[20]

Materials. Lithium metal with high sodium content, obtained from Lithium Corporation of America in the form of rods or wire, was wiped clean, pounded with purified copper powder from Matheson Coleman and Bell, and cut immediately into small chips under a stream of dry, oxygen-free argon.

Pentane was usually purified by passage through a column of molecular sieves and acid-washed alumina, and was then stored over sodium wire.

Argon gas was Matheson, prepurified gas which has been passed through a 1-ft tower of molecular sieves mixed with indicator Drierite to remove water and then through a 3-ft tower of BTS Catalyst, a commercial copper, to remove any oxygen or water.

Bromine, methyl chloroformate, 1,2-dibromoethane, vinyl bromide, vinyl chloride, norbornene, and acrylonitrile were used as obtained from commerical suppliers.

***exo*-2-Norbornyl bromide** was prepared according to Roberts and co-workers[21] in 74% yield. The product was dried over magnesium sulfate and distilled through an 18-in. Holzman column, bp 80–81° (25mm), n^{25}D 1.5128 [lit.[22] bp 84–87° (31mm), n^{25}D 1.5126].

***endo*-2-Norbornyl bromide** was prepared according to Roberts and co-workers[21,23] by selective solvolysis of a mixture of *exo* and *endo* bromides, which was in turn prepared by Diels–Alder reaction of vinyl bromide with cyclopentadiene at 150°, followed by hydrogenation over platinum in ethyl acetate. A mixture shown by nmr to contain equal amounts of the *exo*- and *endo*-norbornyl bromides was allowed to react with 80% aqueous ethanol at 55° for 17.4 hr. The reaction mixture was extracted with methylene chloride to give a solution shown by glpc to contain no *exo* bromide. *endo*-2-Norbornyl bromide was collected by preparative glpc on QF-1 (20% on Gas Chrom). The infrared spectrum agreed qualitatively with that reported.[24] The *exo* and *endo* bromides were most readily distinguished by strong bands (in pure liquids) at 615 and 640 cm^{-1}, respectively, and by the nmr chemical shifts of the 2 protons centered at $\tau = 6.1$ and 5.8 ppm, respectively. The nmr provides a useful quantitative analysis as well (see below).

***exo*-2-Norbornyl chloride** was prepared according to Schmerling[25] from norbornene and hydrogen chloride and purified by distillation. Glpc on QF-1 (15% on Anakrom ABS) at 90° showed only one peak. The infrared spectrum (neat) showed a strong band at 670 cm^{-1}.

***endo*-2-Norbornyl chloride** was prepared by the same kind of sequence used for the bromide condensation of vinyl chloride with cyclopentadiene,[22] reduction over platinum to give an *exo*/*endo* = 0.613 mixture of norbornyl chlorides (nmr analysis), and selective solvolysis in 80% aqueous ethanol at 85° to 48 hr. Distillation of the product through a 3-ft, helix-packed column gave a fraction bp 83–85° (40–41 mm) shown by glpc to contain about 19% of an impurity, which was easily collected (8-ft Carbowax column at 120° used for preparative separation). The impurity was identified as norbornyl ethyl ether by its empirical formula and nmr spectrum, which showed the characteristic -OC_2H_5 multiplets at $\tau = 6.70$ and 8.92 ppm.

Anal. Calcd for $C_9H_{16}O$: C, 77.08; H, 11.50. Found: C, 76.86; H, 11.40.

The major product from the fractional distillation, mp 46.5–47.0°, was identified as *endo*-2-norbornyl chloride by the similarity of its nmr spectrum to that of *endo*-2-norbornyl bromide (C-2 at $\tau = 5.8$ ppm), and by its analysis.

Anal. Calcd for $C_7H_{11}Cl$: C, 64.50; H, 8.49. Found: C, 64.48; H, 8.48.

The infrared spectrum was different from that of the *exo* isomer in all details, and showed a strong band at 680 cm^{-1}.

The ether and norborneol by-products were most conveniently removed on a preparative scale by extraction of a 10% pentane solution of the crude product with concentrated sulfuric acid two or three times. The pentane solution was then washed with water, dried, and distilled to leave a 67.5 yield of white solid, mp 40–41°, bp 80–82° (46–52 mm) [lit.[22] bp 75° (41 mm)]. An nmr analysis showed no *exo* chloride. (The C-2 hydrogens are centered at $\tau = 6.2$ and 5.8 ppm in the *exo* and *endo* chlorides, respectively.)

2-Cyanonorborn-5-ene was prepared as described by Alder and co-workers[26] and separated by fractional distillation through a 4-ft, spinning-band column (10–12 mm) into the *exo* (bp 96°) and *endo* (bp 104°) isomers. The *exo* isomer was only 81% pure according to glpc analysis on QF-1 at 125°. The infrared spectra of the two isomers agreed with those reported,[26] and additional useful medium bands at 858 and 820 cm^{-1} were observed for the *exo* and *endo* isomers, respectively.

***endo*-2-Cyanonorbornane** was prepared from 0.199 mole of *endo*-2-cyanonorborn-5-ene by hydrogenation with a Girdler catalyst in 300 ml of ethanol at 100 psi at room temperature in a glass-lined hydrogenation bomb with a yield of 60.7% (14.67 g). After removal of solvent by distillation, glpc analysis on a QF-1 column at 25° (flow rate 44 cc/min) showed only one peak at 47.0 min. The unsaturated nitriles (*endo* 43.8 min and *exo* 35.4 min) were shown to be absent by glpc. The crude saturated nitrile was then distilled through a Holzman column at 55–60° (2 mm); mp 39.5–41° [lit. bp 90–91° (12 mm),[27] 86° (12 mm);[26] mp 43–44°,[27] 51°[26]].

***exo*-2-Cyanonorbornane** was obtained according to the above procedure in 88.7% yield from 0.202 mole of starting unsaturated nitrile (*exo*/*endo* ratio = 4.41 by glpc). The product was a camphor-like substance melting at hand temperatures, bp 53–55° (2 mm) (lit.[26] mp hand temperatures). The saturated nitriles were not separated by glpc, so that an accurate analysis of *exo*/*endo* ratios was not available, although the hydrogenation should not have affected the stereochemistry at the C-2 position.

***endo*-2-Carbomethoxynorbornane** was prepared from 0.04 mole of *endo*-2-cyanonorbornane in 42.5% yield (lit.[26] 50%). According to Alder's procedure,[26] the nitrile was dissolved in 15 ml of anhydrous methanol and 25 ml of anhydrous ether, and the solution was saturated with dry hydrogen chloride gas at 0° twice, at 24-hr intervals. After the second saturation, the solution was allowed to stand an additional 24 hr and then added to 150 g of crushed ice. After 8 hr, the mixture was worked up by extraction with ether. The ether extracts were washed with saturated sodium bicarbonate and dried over calcium chloride. The ether was removed on a rotary evaporator and the ester distilled, bp 76–77° (11 mm) [lit.[26] 80–82° (12 mm)]. The infrared spectrum (10% in carbon disulfide) of the above pure *endo* ester had a C=O stretch at 1740 cm^{-1} and a band at 745 cm^{-1} (lit.[28] 755 cm^{-1}). The nmr spectrum (carbon tetrachloride–TMS) of pure *endo*-2-carbomethoxynorbornane showed a sharp singlet for the methoxy proton resonance at $\tau = 6.40$ ppm which integrated for 20.2% hydrogen (17.8% calcd).

***exo*-2-Carbomethoxynorbornane** was prepared according to the above procedure in 61.4% yield (lit.[26] 92%) from 7.7 g (0.059 mole) of *exo*-2-cyanonorbornane. For this ester, bp 77° (10 mm) [lit[26] 78–79° (12 mm)], the infrared spectrum (10% in carbon disulfide) contained a C=O stretch at 1735 cm^{-1} and only a slight band at 740 cm^{-1} corresponding to *endo* impurity. The nmr spectrum (carbon tetrachloride–TMS) of the *exo* ester exhibited a sharp singlet for the methoxy proton resonance at $\tau = 6.42$ ppm which integrated for 21.2% hydrogen (17.8% calcd).

Boron trifluoride–methanol methylating reagent was prepared according to Metcalfe and Schmitz[29] by bubbling boron trifluoride gas into 1 l. of reagent grade methanol in a 2-l. erlenmeyer flask at 0° until 300 g of boron trifluoride had been absorbed. The reagent was kept with no noticeable loss of efficiency in the reagent for months at room temperature in an aluminum foil covered flask with a Teflon stopper.

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(20) Microanalyses were done by Mr. Josef Nemeth and associates. Nmr and infrared spectra were done in part by Mr. Dick Johnson and associates. The nmr spectra were measured on a Varian Associates Model A-60 spectrometer. Melting points and boiling points are uncorrected.

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(29) L. D. Metcalfe and A. A. Schmitz, *Anal. Chem.*, **33**, 363 (1961).

2-Carbomethoxynorbornane was prepared according to Sauers and Kwiatkowski[30] from the corresponding 2-norbornane acids by reaction with boron trifluoride–methanol methylating reagent. In a typical run 4 to 20 ml of this reagent was added to 187.4 ml of *exo*/*endo*-2-norbornanecarboxylic acid, and the mixture was heated on a steam bath for 2 min. The mixture was then washed with water and extracted with three volumes of technical grade pentane. After concentration on a Holzman column, 89.2 mg of ester was collected by glpc on a 10-ft Carbowax (20%) column at 180°, flow rate 100 cc/min, in 43.7% yield. The low yield was undoubtedly caused by loss of ester on collection. The reported[30] yields were greater than 90%.

The stereochemistry of the methylation of 2-norbornanecarboxylic acids with boron trifluoride–methanol reagent was determined by saponification of two different *exo*/*endo* isomeric mixtures with 30% methanolic potassium hydroxide at reflux for 3 hr and subsequent reesterification with methylating reagent to obtain the same ratio of isomers as in the starting esters. Predominantly *endo*-2-norbornanecarboxylic acid (infrared analysis) from an *exo*/*endo* ester mixture of 0.094 ± 0.002 was esterified with boron trifluoride–methanol reagent to give an ester mixture of *exo*/*endo* = 0.115. A second sample of *exo*/*endo* esters (0.712) was saponified and reesterified without isolation to give an *exo*/*endo* isomeric ratio of esters equal to 0.711. The *exo*/*endo* ester ratios were determined by glpc as discussed below.

Controls for the product stabilities under the reaction conditions used in the reactions of 2-norbornyllithium are described below, with isopropyllithium used as base. Isopropyllithium was prepared from isopropyl chloride, 7.85 g (0.10 mole), in 50 ml of pentane and 1.50 g (0.216 g-atom) of lithium metal, which had been pounded with copper power, in 80 ml of pentane at reflux as described below for preparation of 2-norbornyllithium in refluxing pentane. The yield of lithium reagent was 36.2% (0.362 *N* in RLi, 100 ml of solution) after filtration and was determined by Gilman's method of double titration, with allyl bromide as a coupling agent (see below).

Control for *exo*-2-Norbornyl Bromide (Carbomethoxylation). To 8.5 ml (3.07 mmoles) of isopropyllithium reagent in pentane, to which 54.5 μl (1 mmole) of bromine had been added, was added at −70° *exo*-2-norbornyl bromide (*endo*/*exo* = 0.035 ± 0.002), 362.5 mg (2.07 mmoles). Immediately after addition of the bromide, 3 ml (39 mmoles) of methyl chloroformate was added. The reaction mixture was worked up as in all other carbomethoxylations described below. The 2-norbornyl bromide was recovered slightly changed (*endo*/*exo* = 0.028 ± 0.003) in 88.2% yield.

Control for *endo*-2-Norbornyl Bromide (Carbomethoxylation). A sample of bromide with *endo*/*exo* = 5.10, 68.6 mg (0.393 mmole), was treated as above with 2.5 ml (0.90 mmole) of isopropyllithium which had been treated previously with 27.3 μl (0.5 mmole) of bromine and then with methyl chloroformate. The bromide was recovered in 94% yield, slightly changed (*endo*/*exo* = 7.14 ± 0.55).

Control for *exo*-2-Norbornyl Bromide (Carbonation). To 3.0 ml (1.09 mmoles) of isopropyllithium in pentane, which had been partially brominated with 5 μl (0.0092 mmole) of bromine, at −70° was added 334.1 mg (1.91 mmoles) of *exo*-2-norbornyl bromide with *endo*/*exo* = 0.035 ± 0.002. Immediately after addition of the bromide, an excess of powdered carbon dioxide (Dry Ice) was added to the stirred solution. The mixture was then worked up as in carbonation–methylation reactions discussed below. The bromide was recovered in 86.4% yield, slightly changed (*endo*/*exo* = 0.027 ± 0.004).

Control for *endo*-2-Norbornyl Bromide (Carbonation). A sample of bromide, with *endo*/*exo* = 2.47, 66.3 mg (0.38 mmole), was treated as above with 2.5 ml (0.90 mmole) of isopropyllithium which had been partially brominated with 27.3 μl (0.5 mmole) of bromine. The bromide was recovered in 59.2% yield, slightly changed (*endo*/*exo* = 3.33 ± 0.15).

Control for *exo*-2-Carbomethoxynorbornane (Carbomethoxylation). To 6.9 ml (2.5 mmoles) of isopropyllithium reagent in pentane at −70° was added 3 ml (39 mmoles) of methyl chloroformate, followed immediately by 379.4 mg (2.46 mmoles) of *exo*-2-carbomethoxynorbornane with *endo*/*exo* = 0.099 ± 0.010. After a standard carbomethoxylation work-up as described below, the ester was recovered in 95.7% yield (2.35 mmoles), essentially unchanged (*endo*/*exo* = 0.081 ± 0.002).

Control for *endo*-2-Carbomethoxynorbornane (Carbomethoxylation). The above procedure was repeated on 3.9 ml (1.4 mmoles) of isopropyllithium and 215.2 mg (1.39 mmoles) of *endo*-2-carbomethoxynorbornane, *endo*/*exo* = 10.63 ± 0.18. The ester was recovered in 94.4% yield (1.31 mmoles), essentially unchanged (*endo*/*exo* = 11.18 ± 0.07).

Control for *exo*-2-Carbomethoxynorbornane (Carbonation). To 3.0 ml (1.09 mmoles) of isopropyllithium reagent at −70° in pentane was added an excess of powdered carbon dioxide (Dry Ice), followed immediately by 316.1 mg (2.05 mmoles) of *exo*-2-carbomethoxynorbornane with *endo*/*exo* = 0.099 ± 0.010. After a standard carbonation–methylation work-up as described below, the ester was recovered in 91.5% yield (1.88 mmoles), essentially unchanged (*endo*/*exo* = 0.091 ± 0.001).

Control for *endo*-2-Carbomethoxynorbornane (Carbonation). The above procedure was repeated on 4.7 ml (1.7 mmoles) of isopropyllithium reagent and 368.8 mg (2.39 mmoles) of *endo*-2-carbomethoxynorbornane with *endo*/*exo* = 10.63 ± 0.18. The ester was recovered in 85.0% yield (2.03 mmoles), essentially unchanged (*endo*/*exo* = 9.86 ± 0.02).

Preparation of 2-Norbornyllithium at 36°. To small strips of high sodium content, lithium metal, freshly prepared as described earlier, in a 300-ml Morton flask under pentane at reflux was added dropwise a pentane solution of 2-norbornyl chloride over periods which varied from 2.4 to 4.5 hr. The reaction mixture was then heated under reflux (condenser between argon inlet and flask) and stirred (with the high-speed side of a two-speed, motor-powered stirrer) for 17–24 hr under a positive pressure of argon. After the mixture was allowed to cool to room temperature, it was transferred without exposure to air into a glass-sintered filtering and receiving apparatus which had been oven dried overnight, flamed out, and flushed with argon at least four times prior to use. The filtering apparatus consisted of a glass-sintered funnel adapted with a ₸ 24/40 female joint at the top and a ₸ 24/40 male joint at the bottom. This was connected to the receiving (or storage) vessel by means of a straight adapter with a side arm. From this side arm *via* a three-way stopcock and manifold, the apparatus could be placed under high or low vacuum or argon. The receiving vessel consisted of a 150-ml capacity, graduated bottle with an off-center ₸ 14/20 female joint and a centered stopcock connected to a female joint on the top of the vessel. The off-centered neck was fitted with a septum which was used for removing samples with a syringe. The top inlet served to shut the apparatus off to the atmosphere, to fill the receiver, or to let argon in during removal of samples in order to prevent air seepage through the septum. The lithium reagent was collected and stored at −70° until the titrations and reactions discussed below could be carried out.

Preparation of 2-Norbornyllithium at 20°. A pentane solution of 2-norbornyl chloride was added dropwise under argon over a period of 1.5 to 3 hr (1.5 hr gave better yields) to a column of lithium metal (treated as described earlier and washed in addition twice with purified pentane) in 70 ml of pentane kept at 20° by means of a water-cooled condenser. The bottom of the column was fitted with a glass-sintered filter disk followed by a stopcock which was connected to the side-arm straight adapter and receiving vessel as described above. The pentane solution was removed at the bottom of the column by means of the stopcock at the same rate as the rate of addition of the chloride to the top of the column. The lithium reagent was collected and stored at −70° until the titrations and reactions discussed below could be carried out.

The conditions required for optimum yields and the nature of the side reactions (mainly Wurtz coupling in a dry, oxygen-free apparatus) were investigated in detail, and these studies are reported elsewhere.[31]

Analysis of Total Lithium Reagent Concentrations. The Gilman double titration[32] with allyl bromide[33] as the coupling agent was used to determine yields of lithium reagents.

Brominations with molecular bromine were carried out with a solution of the lithium reagent at −70° in pentane according to the following procedures. In most of the runs, partial brominations were carried out by addition of a pentane solution of the desired theoretical amount of bromine to a stirred pentane solution of lithium reagent at −70°. (Bromine not in pentane solution solidified at −70° and thus the bromination was prevented or retarded.) After the bromine color disappeared, the second reaction, if any, was carried out. It was found that inverse addition

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[30] R. R. Sauers and G. T. Kwiatkowski, *J. Org. Chem.*, **27**, 4049 (1962).

[31] G. E. Neal, Ph.D. Thesis, University of Illinois, 1966.

[32] H. Gilman and F. K. Cartledge, *J. Organometal. Chem.* (Amsterdam), **2**, 447 (1964).

[33] D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

or an excess of bromine had no effect on the product ratio. In the brominations with excess bromine, the solution was washed with sodium bisulfite followed by water and dried with anhydrous magnesium sulfate prior to concentration of solvent on a Holzman column and glpc analysis.

Carbonations of 2-norbornyllithium were carried out with solid carbon dioxide (crushed Dry Ice) and a solution of the lithium reagent at −70° in pentane according to the following procedures. Since it was shown that the order of addition had no effect on the stereochemical result of this reaction, both methods were used in the carbonations listed above. Solutions of the lithium reagent were added to crushed Dry Ice under pentane and in an argon atmosphere, or crushed Dry Ice was dropped into a stirred solution of the lithium reagent in pentane. The latter method was more inconvenient than the first because bumping occurred occasionally. The solutions were allowed to warm to room temperature, acidified with 2 *N* hydrochloric acid, and treated with boron trifluoride–methanol reagent as discussed above to obtain the methyl ester of 2-norbornanecarboxylic acid for glpc analysis.

Carbomethoxylations of 2-norbornyllithium were carried out with methyl chloroformate and a solution of lithium reagent at −70° in pentane. Since it was again shown that the order of addition of reagents had no effect on the stereochemical result of the reaction, the method of convenience was used in over 90% of the carbomethoxylations; *i.e.*, methyl chloroformate in pentane was added to a stirred solution of the lithium reagent at −70° under argon. The reaction mixture was washed with water to remove any lithium salts, concentrated by distillation of solvent through a Holzman column, and analyzed by glpc.

Bromination with 1,2-dibromoethane of 2-norbornyllithium in pentane at −70° was carried out in the same manner as carbomethoxylation.

Gas chromatographic analyses on the products from norbornyllithium reactions were carried out on an F & M Model 300 chromatograph on a 20-ft QF-1 (5% on Anakrom ABS, 110–120 mesh) 0.25-in., copper column at 75° for 2-norbornyl bromide analyses and at 115° for 2-carbomethoxynorbornane analyses. The temperature was raised to 165° to remove the higher boiling coupling products. Flow rates were varied from 50 to 75 cc/min.

Base-line separations were not obtained for either the esters or the bromides, so that systematic errors due to incorrect assumed peak shapes were evident and probably as high as 20% in unfavorable cases. The errors shown throughout this paper are just average deviations and do not include the systematic errors. It is believed that the qualitative conclusions drawn here are not affected, though the numerical rate constant ratios derived (Table III) can be no more than preliminary approximations.

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π-Electron Participation in the Acetolysis of β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate[1]

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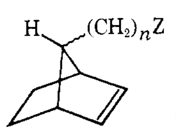
Abstract: The acetolysis of β-(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate in buffered acetic acid at 25° is ~190,000 times as rapid as that of β-(*anti*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate and is accompanied by a 1,3-type hydrogen shift and extensive ion-pair return. The ultimate products of the acetolysis are tetracyclo[$4.3.0.0^{2,4}.0^{3,7}$]nonane, tricyclo[$4.2.1.0^{3,7}$]non-*exo*-2-yl acetate, and tricyclo[$4.3.0.0^{3,7}$]non-*exo*-4-yl acetate. When the acetolysis is stopped after 50% reaction, large amounts of returned tricyclo[$4.2.1.0^{3,7}$]non-*exo*-2-yl *p*-bromobenzenesulfonate can be recovered from the reaction mixture. When the unsaturated brosylate is allowed to stand in unbuffered carbon tetrachloride at 33° it rearranges rapidly to a mixture of tricyclo[$4.3.0.0^{3,7}$]non-*exo*-4-yl and tricyclo[$4.2.1.0^{3,7}$]non-*exo*-2-yl *p*-bromobenzenesulfonates which is converted more slowly into the latter brosylate. The rearrangement does not occur in buffered carbon tetrachloride. It is suggested that the facility of the acetolysis compared to that of β-(3-cyclopentenyl)ethyl *p*-bromobenzenesulfonate (~1500 times at 25°) is probably due to the difference in their respective ground-state energies. An explanation is offered to account for the extensive ion-pair return and the nature of the products.

In a continuation of our search for π-electron participation in the solvolysis of some ω-(7-norbornenyl)alkyl brosylates (**1b**)[2] we have examined the acetolysis of β-(*syn*- and *anti*-7-norbornenyl)ethyl and β-(7-norbornyl)ethyl *p*-bromobenzenesulfonates (**2b**, **3b**, and **4b**, respectively).



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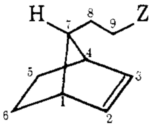

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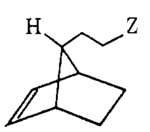

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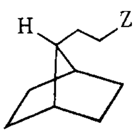

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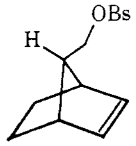
a, Z = OH **b**, Z = OBs **c**, Z = OAc

The β-(7-norbornenyl)ethyl brosylates, **2b** and **3b**, are more suitable for this purpose than the 7-norbornenylmethyl ones, **5** and **6**, examined previously.[2] In



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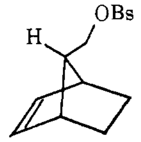

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addition to possessing a leaving group attached to a primary carbon of "normal" hybridization which is symmetrically disposed with respect to a highly strained

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[1] Portions of this work have been presented at (a) the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; Abstracts, p 25P, and (b) the 15th Annual Southeastern Regional Meeting of the American Chemical Society, Charlotte, N. C., Nov 1963; Abstracts, p 79.

[2] R. K. Bly and R. S. Bly, *J. Org. Chem.*, 31, 1577 (1966).