The Addition of Butyllithiums to Benzonorbornadiene and 1,4-Dihydronaphthalene 1,4-*endo*-Oxide

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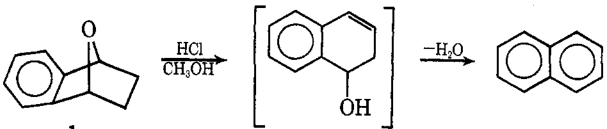
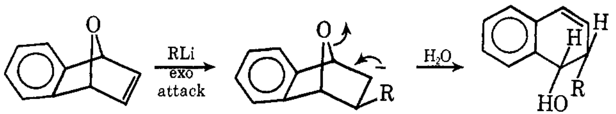
The addition of *n*-butyllithium and *tert*-butyllithium to 1,4-dihydronaphthalene 1,4-*endo*-oxide (**3**) proceeds smoothly with concurrent cleavage to produce, after hydrolysis, the corresponding 1,2-dihydro-*cis*-2-butyl-1-hydroxynaphthalenes **13** and **14**. The cis configuration is the result of initial exo attack and this exo selectivity is observed with additions to benzonorbornadiene (**9**) where a cleavage does not occur. The adducts **13** and **14** are readily dehydrated to produce the corresponding β-butylnaphthalenes **16** and **17**, respectively.

In view of our interest in making certain 2-alkyltetralones, we considered a new approach to these systems based on the isomerization of alkyl derivatives of 1,2,3,4-tetrahydronaphthalene 1,4-*endo* oxide (**1**). It has been noted previously that the endo oxide **1** rearranges in an acidic medium to produce naphthalene,[2] presumably through the intermediate alcohol **2** which readily suffers an acid-catalyzed dehydration.



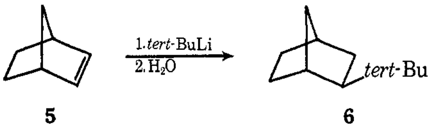
1 **2**

We hoped to introduce an alkyl group by the reaction of an alkyllithium with 1,4-dihydronaphthalene 1,4-*endo*-oxide (**3**), with concomitant cleavage under reaction conditions not conducive to dehydration, to produce 1,2-dihydro-*cis*-2-alkyl-1-hydroxynaphthalenes (**4**).

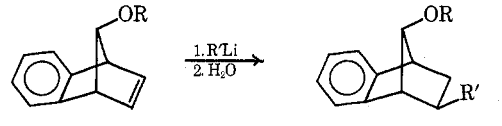


3 **4**

The addition of alkyllithiums to bridged bicyclic systems have been noted previously. Mulvaney and Gardlund[3] have reported the addition of *tert*-butyllithium to norbornene (**5**). The reaction produced the exo addition product **6** and rearrangement or cleavage was not noted. Wittig and Otten[4] have reported the addition of isopropyllithium and *tert*-butyllithium to *anti*-7-methoxybenzonorbornadiene (**7**) and *anti*-7-*tert*-butoxybenzonorbornadiene (**8**). The configuration of the adducts was thought to be exo but this was not rigorously established.



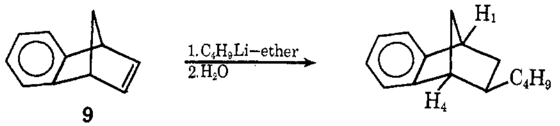
5 **6**



7,R = $CH(CH_3)_2$
8,R = $C(CH_3)_3$

R′ = $CH(CH_3)_2$ or $C(CH_3)_2$

We initiated the present work by examining the stereochemistry of the reaction of *n*-butyllithium, *sec*-butyllithium, and *tert*-butyllithium with benzonorbornadiene (**9**). In agreement with Mulvaney's observation, an exo stereoselectivity was observed. This assignment was made by comparing the widths at half-height for the H_1 and H_4 protons[5] in the nmr spectra (Table I). A typical bridgehead exo vicinal coupling is missing for H_4 but present for H_1.[6]



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10, C_4H_9 = *n*-butyl
11, C_4H_9 = *sec*-butyl
12, C_4H_9 = *tert*-butyl

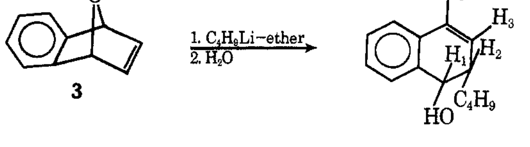
TABLE I

NMR DATA[5] FOR THE ADDUCTS **10**, **11**, and **12**[a]

Adduct	Chemical shift of H_1 and width at half-height, Hz	Chemical shift of H_4 and width at half-height, Hz
exo-5-*n*-Butylbenzonorbornene (**10**)	δ 3.20, 5.5	δ 2.95, 3.0
exo-5-*sec*-Butylbenzonorbornene (**11**)	δ 3.16, 6.0	δ 2.93, 3.0
exo-5-*tert*-Butylbenzonorbornene (**12**)	δ 3.23, 6.0	δ 3.10, 3.5

[a] Solvent CCl_4.

The reaction of the oxide **3** with *tert*-butyllithium and *n*-butyllithium confirmed the hoped for ring opening. The oxide system **3** reacted almost instantly with the butyllithiums and is much more reactive than benzonorbornadiene (**9**) (see Experimental Section).[7,8] This



3

13, C_4H_9 = *tert*-butyl
14, C_4H_9 = *n*-butyl

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[1] National Science Foundation Undergraduate Research Participant, 1970.

[2] G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

[3] J. E. Mulvaney and Z. G. Gardlund, *J. Org. Chem.*, **30**, 917 (1965).

[4] G. Wittig and J. Otten, *Tetrahedron Lett.*, 601 (1963); G. Wittig and E. Hahn, *Angew. Chem.*, **72**, 781 (1960).

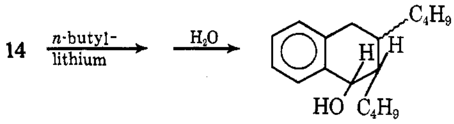
[5] Chemicals shifts are relative to TMS (60 MHz).

[6] S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967).

[7] P. D. Bartlett, S. Friedman, and M. Stiles, *J. Amer. Chem. Soc.*, **75**, 1771 (1953).

[8] (a) P. D. Bartlett, S. J. Tauber, and W. P. Weber, *ibid.*, **91**, 6362 (1969); (b) A. W. Langer, *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965); (c) G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964); (d) H. E. Zieger and E. M. Laski, *Tetrahedron Lett.*, 3801 (1966).

addition–cleavage proceeded essentially quantitatively for the production of **13**, but the yields of **14** were lower owing to the subsequent reaction with a second equivalent of *n*-butyllithium to produce the diadduct **15**. This problem, nonexistent with **13**, can be minimized by the use of 1 equiv of *n*-butyllithium.



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The nmr parameters for the alkyllithium adducts **13** and **14** are listed in Table II. The $J_{1,2}$ vicinal coupling values of 4.1 and 5.0 Hz are in agreement with a slightly skewed, cis arrangement[9] for the hydroxyl and butyl groups about C_1 and C_2. A cis relationship between these two groups results from the preferential exo attack on the oxide **3** and this observation is consistent with the noted preference for exo attack on benzonorbornadiene (**9**). Exo attack would seem very likely with **3** owing to the possibility of prior coordination of the alkyllithium with the bridged oxygen atom.

TABLE II

NMR DATA

Chemical Shifts from TMS,[a,b] Ppm

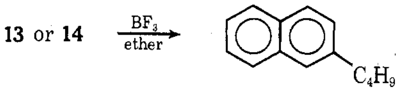
Compd	Aromatic protons	Butyl protons	H_1	H_2	H_3	H_4
13	7.1–7.3	1.13 s	4.53 d	2.15 m	5.96 dd	6.56[c] dt
14	6.8–7.3	2.7–0.9 m	4.48 d	*d*	5.72 dd	6.36 dd

Coupling Constants, Hz

Compd	$J_{1,2}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$
13	*Ca.* 4.1[e]	1.8	3.0	9.7
14	5.0	3.3	2.0	9.5

[a] Solvent CCl_4. [b] Reported for the center of an unsymmetrical multiplet. [c] A second long-range coupling of 1.8 Hz observed. [d] Under methylene envelope. [e] Finer splitting also observed.

The alcohols **13** and **14** were readily dehydrated under acidic conditions to produce the corresponding β-butylnaphthalenes **16** and **17**. This offers a potentially useful route to β-alkylnaphthalenes, products that are not always readily accessible by other means.



16, C_4H_9 = *tert*-butyl
17, C_4H_9 = *n*-butyl

Experimental Section

Analytical.—Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were obtained on a Varian A-60D spectrometer with tetramethylsilane as an internal standard.

Reagents.—*n*-Butyllithium (22% in *n*-hexane), *sec*-butyllithium (2 *M* *n*-hexane), and *tert*-butyllithium (2 *M* *n*-pentane) were obtained from Alfa Inorganics Inc. and were used without further purification. Benzonorbornadiene (**9**) was prepared by the method of Wittig and Knauss.[10] 1,4-Dihydronaphthalene 1,4-*endo*-oxide (**3**) was synthesized according to the procedure of Fieser and Haddadin.[11]

Addition of the Butyllithiums to Benzonorbornadiene (**9**).—The general procedure used is described for the formation of *exo*-5-*n*-butylbenzonorbornene (**10**) from **9**. Benzonorbornadiene (**9**), 2.10 g (14.8 mmol), and 10 ml of dry ethyl ether were placed in a reaction flask under a nitrogen atmosphere. *n*-Butyllithium, 25 ml (61 mmol), was added to the stirred reaction mixture over a period of 10 min. Stirring was continued for 4.5 days at room temperature. About 30 ml of water was then added and the reaction mixture was stirred for another 0.5 hr. The ether layer was separated and washed with a saturated sodium bicarbonate solution. The ether layer was dried over anhydrous magnesium sulfate and solvent was removed under reduced pressure. A nmr spectrum indicated the crude product to be almost exclusively **10**. Two short-path distillations (oil bath temperature 98°, 0.05 mm) were performed on the crude product. A colorless oil, 1.30 g (43%), of pure *exo*-5-*n*-butylbenzonorbornene (**10**) was obtained.

Anal. Calcd for $C_{15}H_{20}$: C, 89.95; H, 10.05. Found for **10**: C, 89.99; H, 10.13. Found for **11**: C, 90.08; H, 10.06. Found for **12**: C, 89.97; H, 10.19.

1,2-Dihydro-*cis*-1-hydroxy-2-*tert*-butylnaphthalene (**13**).—1,4-Dihydronaphthalene 1,4-*endo*-oxide (**3**), 0.250 g (1.74 mmol), was dissolved in 50 ml of anhydrous ether under a nitrogen atmosphere. *tert*-Butyllithium, 3.0 ml (6.0 mmol), was added and the solution was stirred at room temperature for 1 hr. The excess *tert*-butyllithium was destroyed by the addition of 25 ml of water and the ether layer was removed and dried. An almost quantitative yield of essentially pure **13** was obtained. This material was sublimed twice at 50° (0.2 mm) to yield crystalline **13**, mp 75–76°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.21; H, 9.11.

1,2-Dihydro-*cis*-1-hydroxy-2-*n*-butylnaphthalene (**14**).—1,4-Dihydronaphthalene 1,4-*endo*-oxide (**3**), 0.319 g (2.21 mmol), was dissolved in 50 ml of dry ether under a nitrogen atmosphere. *n*-Butyllithium, 1.0 ml (2.4 mmol), was added and the solution was stirred for 15 min. The work-up was as with formation of **13** except that a greater difficulty was experienced in isolating pure **14**. The recovered product was primarily **14** (85–90%) with small amounts of the starting olefin **3** and the diadduct **15** present. A sample of pure **14** was obtained by removing unreacted **3** by a short-path distillation (a sublimation apparatus was used) at 40° (0.2 mm) and then taking the center cut distilling at 60° (0.2 mm). This procedure was repeated four times and produced an analytical sample of a colorless oil.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.26; H, 8.85.

1,2,3,4-Tetrahydro-1-hydroxy-2,3-di-*n*-butylnaphthalene (**15**).—The diadduct **15** was obtained in the same manner as the monoadduct **14** except that an excess quantity (3 equiv) of *n*-butyllithium was used and the reaction was allowed to go for 2 hr. A small amount of material was removed at 50° (0.2 mm) and the remainder was sublimed at 85° (0.2 mm) to yield a crystalline material, mp 65–70°. Repeated sublimations did not sharpen the melting point and the product is probably a mixture of the cis and trans isomers about C-2 and C-3. The nmr spectrum integrates correctly for the proposed structure but does not define the stereochemistry at C-3. Only one signal for H_1 is observed, δ 4.67, with $J_{1,2}$ = *ca.* 4.5 Hz, and the two benzylic hydrogens are centered at δ 2.64.

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.89; H, 10.93.

β-*tert*-Butylnaphthalene (**16**).—The dihydronaphthalene system **13** was readily dehydrated in a dilute ether solution by adding a few drops of boron trifluoride etherate and stirring for 10 min. A work-up was accomplished by the addition of water, washing with a 10% sodium bicarbonate solution, and drying the ether extracts. The recovered product was essentially pure **16**. A short-path distillation, 45° (0.2 mm), produced an analytical sample.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.45; H, 8.76.

β-*n*-Butylnaphthalene (**17**).—The dihydronaphthalene system

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[9] F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961), and references cited therein.

[10] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

[11] L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965).

14 was dehydrated and purified to produce **17** in the same manner used for the preparation of **16** from **13**.

Anal. Calcd for $\mathrm{C_{14}H_{16}}$: C, 91.25; H, 8.75. Found: C, 91.09; H, 8.82.

Registry No.—**3**, 573-57-9; **9**, 4453-90-1; **10**, 30953-00-5; **11**, 30882-79-2; **12**, 30882-80-5; **13**, 30882-81-6; **14**, 30882-82-7; **15**, 30882-83-8; **16**, 2876-35-9; **17**, 1134-62-9.

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Synthetic Reactions by Complex Catalysts. XX. Copper(I)-Catalyzed Formimidation of Amine, Alcohol, and Amide by Vinyl Isocyanide

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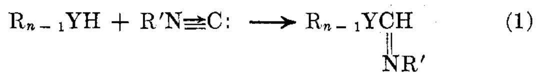
In the presence of cuprous oxide catalyst, vinyl isocyanide (VIC) easily reacts with amine, alcohol, thiol, and several *N*-alkyl derivatives of carboxylic amide, carbamate, urea, and thiourea. The reaction with primary amine occurs in two courses according to the VIC–amine feed ratio; the one leads to **4** by the twofold formimidation and the other to the production of a mixture of **6** and **7**. The reaction of VIC with *N*-alkylamide produces the formimidation product **11**. Similarly, the reactions of VIC with *N*-alkyl derivatives of carbamate, urea, and thiourea proceed at room temperature to give the corresponding *N*-vinylformimidate derivatives (eq 5). In the reaction with alcohol, two consecutive reactions take place. The first reaction is formimidation and the second one is the 1,4 addition of alcohol to the formimidation product (eq 9). The product is determined by the VIC–alcohol feed ratio and the reaction temperature. The reaction with thiol is similar to that with alcohol.

In previous papers[1–5] we have described the copper-catalyzed reactions of various $\mathrm{R_{n-1}YH}$ compounds with isocyanide to give α-addition products (eq 1).



$$\mathrm{R_{n-1}YH} + \mathrm{R'N{\equiv}C\!:} \longrightarrow \mathrm{R_{n-1}Y\underset{\underset{NR'}{\|}}{C}H} \qquad (1)$$

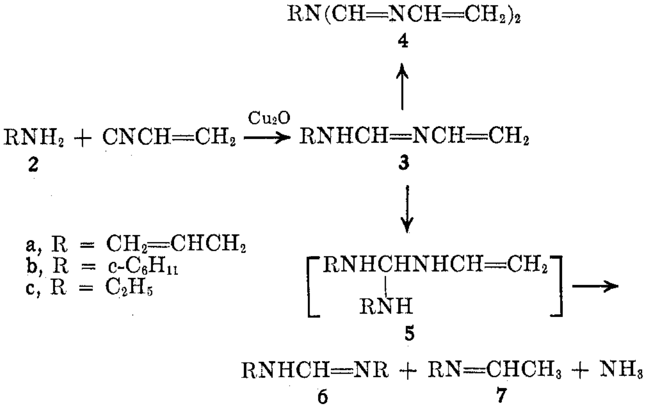
1

$$\mathrm{Y} = \mathrm{N, P, O, S, Si}$$

The products of these reactions can be regarded as the derivatives of a hypothetical species of formimidic acid, HOC(=NR)H. We wish to propose a general name of "formimidation" for these reactions. In this paper we report the extension of these reactions to vinyl isocyanide (VIC).

Results and Discussion

Reaction with Amines.—In the combination of VIC–secondary amine, (*e.g.*, piperidine), the usual formimidation takes place at room temperature to produce *N*-vinylformamidine in quantitative yields (Table I).



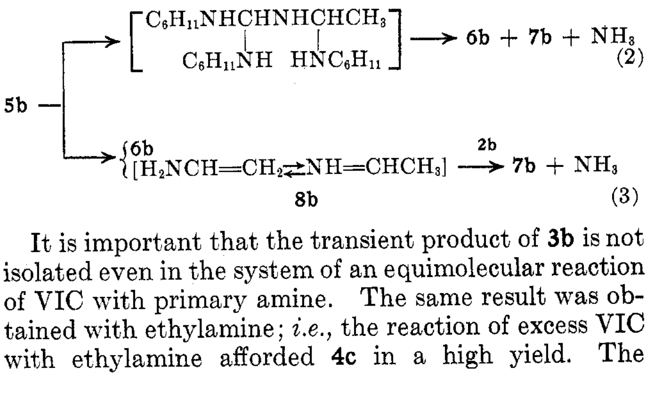
$$\mathrm{RN(CH{=}NCH{=}CH_2)_2}\ \ \mathbf{4}$$

$$\underset{\mathbf{2}}{\mathrm{RNH_2}} + \mathrm{CNCH{=}CH_2} \xrightarrow{\mathrm{Cu_2O}} \underset{\mathbf{3}}{\mathrm{RNHCH{=}NCH{=}CH_2}}$$

a, R = $\mathrm{CH_2{=}CHCH_2}$
b, R = c-$\mathrm{C_6H_{11}}$
c, R = $\mathrm{C_2H_5}$

$$\left[\mathrm{RNH\underset{\underset{RNH}{|}}{C}HNHCH{=}CH_2}\right]_{\mathbf{5}} \longrightarrow \underset{\mathbf{6}}{\mathrm{RNHCH{=}NR}} + \underset{\mathbf{7}}{\mathrm{RN{=}CHCH_3}} + \mathrm{NH_3}$$

The $\mathrm{Cu_2O}$-catalyzed reactions of VIC with primary amines, however, give three products (**4**, **6**, and **7**) depending upon the VIC–amine feed ratio and the nature of the amine. The equimolecular reaction of VIC with cyclohexylamine (**2b**) produces three products, **4b**, **6b**, and **7b**, in a ratio of 0.4:1:1.3. The reaction of 2:1 VIC–**2b** gives only **4b**, whereas that of 1:4 VIC–**2b** affords **6b** and **7b**. The formation of **4b** is explained by the secondary reaction of the normal formimidation product **3b**, *i.e.*, the insertion of VIC into >NH of **3b**. The formations of **6b** and **7b** are rationalized by a scheme of the reaction of **3b** with amine. The addition of **2b** to the >C=N– bond of **3b** leads to an unstable triamine **5b**, whose decomposition produces **6b** and **7b**. The decomposition of **5b** may possibly take either of the following two courses. The one is the addition of amine to **5b**, which is followed by the cleavages of an unstable polyamino compound (eq 2). The other is the cleavage of **5b**, producing **6b** and aldimine (**8b**), which is followed by the reaction of **8b** with **2b** (eq 3).



$$\mathbf{5b} \longrightarrow \left[\mathrm{C_6H_{11}NH\underset{\underset{C_6H_{11}NH}{|}}{C}HNH\underset{\underset{HNC_6H_{11}}{|}}{C}HCH_3}\right] \longrightarrow \mathbf{6b} + \mathbf{7b} + \mathrm{NH_3} \qquad (2)$$

$$\mathbf{5b} \longrightarrow \left\{\begin{matrix}\mathbf{6b}\\ \underset{\mathbf{8b}}{[\mathrm{H_2NCH{=}CH_2 \rightleftarrows NH{=}CHCH_3}]}\end{matrix}\right. \xrightarrow{\mathbf{2b}} \mathbf{7b} + \mathrm{NH_3} \qquad (3)$$

It is important that the transient product of **3b** is not isolated even in the system of an equimolecular reaction of VIC with primary amine. The same result was obtained with ethylamine; *i.e.*, the reaction of excess VIC with ethylamine afforded **4c** in a high yield. The

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(1) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Lett.*, 6121 (1966).

(2) T. Saegusa, Y. Ito, and S. Kobayashi, *ibid.*, 935 (1968).

(3) T. Saegusa, Y. Ito, S. Kobayashi, N. Takeda, and K. Hirota, *ibid.*, 1273 (1967).

(4) T. Saegusa, S. Kobayashi, K. Hirota, Y. Okumura, and Y. Ito, *Bull. Chem. Soc. Jap.*, **41**, 1638 (1968).

(5) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *J. Amer. Chem. Soc.*, **89**, 2240 (1967).