The separation of 2-butanol and methyl-*t*-butylcarbinol from *d*-isoborneol was accomplished by first distilling through a six-inch Vigreux column and subsequently fractioning through a 23-plate spinning band column. Both alcohols were found to be optically inactive. It is possible that in the procedure employed by Bothner-By,[1] separation of 2-butanol and methyl-*t*-butylcarbinol from small quantities of optically active material was incomplete and consequently caused the observed positive rotation.[2]

In a recent communication, Eliel[3] has presented evidence for a possible disporportionation step in the reduction of 3,3,5-trimethylcyclohexanone with lithium aluminum hydride. If this is of general consequence in the reduction of ketones to secondary alcohols, perhaps the production of racemic alcohols from ketones with lithium aluminum hydride–*d*-camphor is indicative of attack by AlH_4^- rather than $Al(OR)_2H_2^-$. Thus during the reduction of two equivalents of *d*-camphor by one equivalent of lithium aluminum hydride, the initially formed $Al(OR)H_3^-$ can conceivably be transformed to AlH_4^- *via* a disproportionation step.[3] Since $Al(OR)H_3^-$ is not as effective as reducing agent,[4] AlH_4^- could act as the reducing species even in the presence of a substantial quantity of alkoxyhydride anion.

Experimental

Reduction of 2-Butanone.—A solution of 30 g. (0.2 mole) of *d*-camphor in 50 ml. of ether was dropped with stirring over a 0.5-hr. period into a solution of 3.8 g. (0.2 mole) of lithium aluminum hydride in 300 ml. of ether. This was followed by a 0.5-hr. addition of 15 ml. (0.2 mole) of 2-butanone in 50 ml. of ether. To the above mixture there was added 100 ml. of 17% hydrochloric acid followed by several grams of sodium chloride so as to facilitate separation of the ether layer. The organic phase was dried over calcium chloride and subsequently with calcium hydride. The ether was distilled from a mixture on a steam bath and 15 ml. of xylene added to the residue. Distillation through a 6-in. Vigreux column followed by two fractionations through a 23-plate spinning band column afforded 5 ml. of 2-butanol; b.p. 99° (750 mm.), $n^{25°}$ 1.3952, $[\alpha]^{25}{}_{D}$ 0°.

Reduction of Pinacolone.—Pinacolone, 20 g. (0.2 mole), was reduced in a manner identical to that of 2-butanone. After treatment with 100 ml. of 17% hydrochloric acid the ether solution was dried over calcium chloride and the solvent removed by distillation. To the residue was added 15 ml. of decalin and the methyl-*t*-butylcarbinol distilled through a 6-in. Vigreux column. Two subsequent fractionations through a 23-plate spinning band column gave 7 ml. of methyl-*t*-butylcarbinol; b.p. 119–119.5 (748 mm.), n^{25} 1.4127, $[\alpha]^{25}{}_{D}$ 0°.

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[2] In a recent private communication, Dr. Bothner-By has expressed his agreement with us concerning the absence of asymmetric induction in the *d*-camphor–lithium aluminum hydride reduction of 2-butanone and pinacolone.

[3] E. L. Eliel and H. Haubenstock, Abstracts of papers presented at 141st National Meeting, American Chemical Society, p. 11-O.

[4] H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958).

Acidity of Hydrocarbons. VI. Metalation of Norbornadiene with Butyllithium[1]

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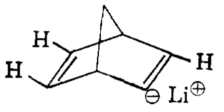
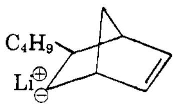
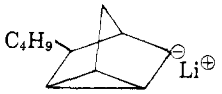
Wittig and Hahn[3] have reported that the reaction of norbornadiene with equimolar butyllithium gives products expected from the ion-pairs, I, II, and III. We have performed similar experiments in order to obtain evidence relating to the relative acidities of the various hydrogens in norbornadiene. Of particular interest is the relative mobility of the 7-hydrogens (bridge) because simple MO calculations predict no delocalization energy for the anion IV.



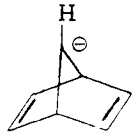
I



II



III



Norbornadiene was allowed to react with excess butyllithium in refluxing ether–heptane. After quenching with deuterium oxide, the recovered norbornadiene was studied by infrared and n.m.r. No evidence was obtained for significant abstraction of a 7-hydrogen, in qualitative agreement with the molecular orbital prediction.

The reaction mixture had typically a magenta color (λ_{max} 560 mμ). The product mixture as analyzed by gas chromatography contained norbornadiene and high-boiling materials, presumably the butylated products reported by Wittig and Hahn.[3] Norbornadiene as separated by gas chromatography showed vinyl deuterium in amounts depending on the duration of the reaction (Table I). In the product of the ten-hour reaction the

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[1] Paper V, A. Streitwieser, Jr., D. E. Van Sickle, and L. Reif, *J. Am. Chem. Soc.*, **84**, 258 (1962). This research was supported in part by an Air Force Grant, AFOSR-62-175.

[2] Alfred P. Sloan Fellow, 1958–1962.

[3] G. Wittig and E. Hahn, *Angew. Chem.*, **72**, 781 (1960).

n.m.r. spectrum showed the bridge and vinyl hydrogens as triplets and the bridgehead hydrogens as a sextet compared to the septet found for the last hydrogens in the starting norbornadiene. The results demonstrate no significant exchange of bridge hydrogens but do show almost complete metalation of a vinyl position. Although the final yield is small, the availability of norbornadiene makes this procedure acceptable as a preparation of norbornadiene-2-*d*.

TABLE I

DEUTERIUM CONTENT OF NORBORNADIENE

Hydrogens	τ^a	Number of H's by n.m.r. areas: 0.5-Hr. reaction time[b]	Number of H's by n.m.r. areas: 10-Hr. reaction time[c]
7 (bridge)	8.07	2.0	1.99
1,4 (bridgehead)	6.48	2.00	2.00
2,3,5,6 (vinyl)	3.35	3.56	3.08

[a] Assigned by Story (ref. 4). [b] Yield >50%. [c] Yield 11%.

When the deuterium oxide used to quench the reaction mixture contained tritiated water, the recovered norbornadiene showed substantial tritium incorporation when examined with a proportional flow counter associated with the gas chromatograph. In contrast, recovered norbornene, when treated in the same fashion for nine hours, showed only traces of tritium incorporation. The n.m.r. spectrum showed 1.96 vinyl hydrogens. In this type of metallation exchange reaction, the vinyl hydrogens of norbornene are clearly much less acidic than those of norbornadiene. One possible explanation is that each double bond in norbornadiene exerts an important inductive effect to enhance the acidity of the other.

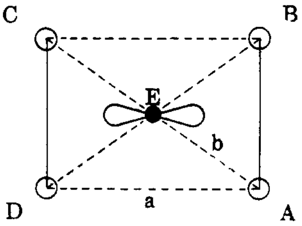
Experimental

Commercially available butyllithium in hydrocarbon solvents, from either Foote or Lithium Corporation of America, was used. Norbornadiene from Shell was found to be 98–99% pure by vapor phase chromatography and was not purified further. N.m.r. spectra were run on a Varian A-60 n.m.r. spectrometer.

Norbornadiene (2.8 g., 30 mmoles) was added to a solution of butyllithium (50 mmoles) in 50–75 cc. ether–heptane. The ether had been distilled from lithium aluminum hydride, and a positive pressure of nitrogen was maintained over the reaction mixture. After allowing the mixture to reflux the appropriate length of time, 2 cc. of deuterium oxide was added dropwise, and reflux was continued for at least 1 hr. After separation from inorganic materials and drying over magnesium sulfate, the reaction mixture was distilled. The fraction boiling at 85–95° could be separated on a Carbowax v.p.c. column to afford norbornadiene.

Simple LCAO Calculations

The model assumed is given as V:



The bond integrals are taken as $\mathbf{H}_{AB} = \beta$, $\mathbf{H}_{AD} = a\beta$, $\mathbf{H}_{AE} = b\beta$. All coulomb integrals, $\mathbf{H}_{rr} = \alpha$. Overlap integrals are neglected as usual. Four symmetry orbitals can be constructed from the equivalent atomic orbitals, φ_A, φ_B, φ_C, φ_D:

$$\varphi_1 = {}^1/_2\,(\varphi_A + \varphi_B + \varphi_C + \varphi_D)$$

$$\varphi_2 = {}^1/_2\,(\varphi_A + \varphi_B - \varphi_C - \varphi_D)$$

$$\varphi_3 = {}^1/_2\,(\varphi_A - \varphi_B - \varphi_C + \varphi_D)$$

$$\varphi_4 = {}^1/_2\,(\varphi_A - \varphi_B + \varphi_C - \varphi_D)$$

Because φ_E is antisymmetric to a vertical plane through *E*, this orbital interacts only with φ_2. The five possible MO's are derived from three first-order and one second-order determinant giving the energy levels:

$$\epsilon_5 = \alpha - (1 + a)\,\beta$$

$$\epsilon_4 = \alpha - (1 - a)\,\beta$$

$$\epsilon_3 = \alpha - \frac{\lambda - (1 - a)}{2}\,\beta \qquad \lambda = \sqrt{(1 - a)^2 + 16b^2}$$

$$\epsilon_2 = \alpha + \frac{\lambda + (1 - a)}{2}\,\beta$$

$$\epsilon_1 = \alpha + (1 + a)\,\beta$$

In setting this order we assume $a < 1$. The π-energy of the cation corresponding to IV is given as: $E^+ = 2\epsilon_1 + 2\epsilon_2$. For any value of $b > 0$, the bonding energy is greater than 4β; that is, two isolated double bonds; hence, this cation is expected to have stabilization energy. However, the energy of the anion, V, is given as: $E^- = 2\epsilon_1 + 2\epsilon_2 + 2\epsilon_3$. All of the *a* and *b* terms vanish identically leaving $E^- = 4\alpha + 4\beta$; that is, the energy of two isolated double bonds. It should be noted that the anion has no stabilization relative to the starting hydrocarbon for any reasonable value of *a*.[5]

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[4] P. R. Story, *J. Am. Chem. Soc.*, **82**, 2085 (1960).

[5] This statement is true for any set of values of *a* and *b* such that $0 \leq b \leq \frac{1}{\sqrt{2}}(1 - a)$. For other values ϵ_4 becomes larger than ϵ_3 and $E^- = 2\epsilon_1 + 2\epsilon_2 + 2\epsilon_4$. In this case stabilization of the anion is predicted; however, such values of *a* and *b* are physically unrealistic.