Organometallic Chemistry. VII. The Reactions of Amylsodium with Norbornene, *endo*-5-Hydroxymethylnorbornene, Nortricyclene, and Norbornadiene^{1,2}

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Norbornene provided norbornene-2-carboxylic acid in good yield after treatment with amylsodium followed by carbon dioxide and mineral acid. Reaction of the intermediate 2-sodionorbornene with benzaldehyde gave rise mainly to benzyl benzoate and only a small amount of an adduct whose structure remains undefined. Similarly, treatment of nortricyclene and 5-hydroxymethylnorbornene with amylsodium followed by carbonation and acidification, afforded nortricyclene-1-carboxylic acid and 6-hydroxymethylnorbornene-2-carboxylic acid, respectively. The latter acid spontaneously lactonized on catalytic reduction. Cyclopentadienylsodium and acetylene were produced when norbornadiene reacted with amylsodium. Carbonation of this reaction mixture gave a nearly quantitative yield of dicyclopentadiene dicarboxylic acid. Pertinent infrared, ultraviolet, and nuclear magnetic resonance spectral data on the acids and their various derivatives are presented and discussed.

A characteristic property of sodium alkyls is their ability to promote metal--hydrogen exchange reactions with a variety of hydrocarbon substrates.⁵ These reactions can be considered as acid--base reactions in which the metal alkyl serves as a powerful base and the hydrocarbon substrate as a weak protic acid (eq. 1). When R

$$RNa + R'H \longrightarrow RH + R'Na$$
(1)

is a saturated alkyl groups, R'H may represent an aromatic or alkylaromatic hydrocarbon, an olefin, or a cyclopropane. In each case the reaction is essentially irreversible since RH, a saturated alkane, is much the weaker of the two acids present.⁶ A simple example is illustrated in eq. 2 by the reaction of propylene with amylsodium to produce *n*-pentane and the resonance-stabilized allylsodium.⁷ The pioneering work of Mor-

$$n - C_{b}H_{11} - Na^{+} + CH_{2} \Longrightarrow CHCH_{3} \longrightarrow \\ n - C_{b}H_{12} + [CH_{2} - CH - CH_{2}] - Na^{+}$$
(2)

ton on olefin metalation led to a useful structure-reactivity generalization⁷ in which the relative ease of proton removal from an olefin may be summarized.



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(4) Frederick Gardner Cottrell Fellow, 1960-1961, 1962-1963; National Science Foundation Cooperative Fellow, 1961-1962; Petroleum Research Fund Fellow, 1963. Portions of this paper have been adapted from a thesis presented by R. S. M. to the Department of Chemistry, Ohio State University, winter, 1963, in partial fulfillment of the requirements for the M.S. degree. For preliminary communications see ref. 2d and f.

(5) R. A. Benkeser, D. J. Foster, D. M. Sauve, and J. F. Nobis, *Chem. Rev.*, 57, 867 (1957).

(6) Only in cases where the metal is potassium has the exchange been observed when both R and R' are saturated alkyl groups.^{2b} Cyclopropanes are an exception; however, these are well known to possess a degree of olefinic character. A report^{6a} that decalin could be metalated with amylsodium was subsequently retracted^{6b}: (a) A. A. Morton, et. al., J. Am. Chem. Soc., **64**, 2250 (1942); (b) A. A. Morton and A. E. Brachman, *ibid.*, 2973 (1954), footnote 15.

(7) A. A. Morton, M. L. Brown, M. E. T. Holden, R. L. Letsinger, and E. E. Magat, *ibid.*, **67**, 2224 (1945).

That is allylic methyl hydrogens are easier to abstract than allylic methylene hydrogens, which in turn are easier to abstract than vinyl hydrogens. More recently, a penetrating study by Broaddus^{8a} has modified this reactivity order and demonstrated that resonance stabilization of the conjugate base is not necessarily the predominant factor governing the site of olefin metalation by sodium alkyls. Hybridization and polarizability effects conjoin with the resonance effect to produce the following revised order.^{8b} Similar effects

$$C = C - CH_2 > C = CH > -CH - C = C > -C = C$$

are very likely operative in the metalation of alkylaromatic hydrocarbons where ring and benzylic metalation are competitive, and, although ring metalation is favored, rearrangement to the more stable benzylic salt ensues.⁹

The metalation of cyclic olefins (excepting cyclopentadiene and its benzo derivatives) has been reported only a few times. These reactions, in which the olefin is treated with amylsodium, the mixture is carbonated, and the resultant carboxylic acids are isolated and characterized, are summarized in eq. 3–7. 1,4-Dihydronaphthalene^{10a} (eq. 3) and 1,4-cyclohexadiene^{10b} (eq. 4) both illustrate the ease with which the six-membered ring becomes aromatized by the elimination of sodium hydride from the intermediate cyclohexadienylsodium. (Formic acid is produced by carbonation of sodium hydride.) 1-Methylcyclohexene¹¹ provided the aromatization products, homoisophthalic acid¹² and formic acid, as well as 2-methylenecyclohexanecarboxylic acid,

(8) (a) C. D. Broaddus, T. L. Logan, and T. J. Flautt, J. Org. Chem., 28, 1174 (1963). (b) In this, as in the previously mentioned reactivity series, emphasis is placed on the immediate functional environment of the acidic proton. Other factors which will affect olefin acidity, such as the number and kinds of substituents on the resulting metal derivative, are assumed to cancel.

(9) (a) R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, J. Am. Chem. Soc., 85, 3984 (1963); (b) R. A. Benkeser, A. E. Trevillyan, and J. Hooz, *ibid.*, 84, 4971 (1962); (c) A. A. Morton and C. E. Claff, *ibid.*, 76, 4935 (1954); (d) A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., *ibid.*, 65, 1339 (1943).

(10) (a) R. Paul and S. Tchelitcheff, Bull. soc. chim. France, 15, 108 (1948); (b) R. Paul and S. Tchelitcheff, Compt. rend., 239, 1222 (1954).

(11) A. A. Morton and R. A. Finnegan, J. Polymer Sci., 38, 19 (1959).

(12) Homoisophthalic acid is known to result from the dimetalation of toluene, followed by carbonation. 9d

⁽²⁾ Previous papers in this series: (a) VI, R. A. Finnegan, Tetrahedron Letters, 13, 851 (1963); (b) V, ibid., 7, 429 (1963); (c) IV, ibid., 26, 1303 (1962); (d) III, R. A. Finnegan and R. S. McNees, ibid., 17, 755 (1962); (e) II, R. A. Finnegan, Chem. Ind. (London), 895 (1962); (f) I, R. A. Finnegan and R. S. McNees, ibid., 1450 (1961).

$$\begin{array}{c} & \longrightarrow \\ & & & \\ &$$

$$\bigcirc \rightarrow \bigcirc + HCO_2H \qquad (4)$$

$$\underbrace{\bigcirc}_{CO_2H} \rightarrow \underbrace{\bigcirc}_{CO_2H} + \underbrace{O_2H} + \underbrace{O$$

$$\bigcirc \rightarrow \bigcirc_{\rm CO_2H} \tag{6}$$

derived from the simple intermediate allylic species¹³ (eq. 5). Finally, the metalation of cyclohexene and cyclopentene provides an interesting example of the subtle effects which sometimes determine the site of metalation. Cyclohexene¹¹ afforded, in "normal" fashion, the β - γ -unsaturated acid (eq. 6) resulting from an allylic sodium intermediate, whereas cyclopentene¹¹ was transformed into the α - β -unsaturated acid (eq. 7) via a vinylsodium intermediate. Presumably, the resonance energy gained by the formation of an allylic ion is offset by the increase in strain which would accompany the introduction of a third trigonal center into the five-membered ring. The possibility that cyclohexene was also metalated in a kinetically controlled step at a vinyl position, followed by rearrangement to form the allylic ion, appears to be ruled out by the observations of Broaddus⁸ on the stability of vinylsodium compounds.

In recent years a wide variety of reactions has been carried out using norbornene as the unsaturated substrate. The rigid geometry and increased strain energy of this molecule frequently confer a unique new definition to many previously known olefin reactions. For these reasons we became interested in the application of the metalation reaction to norbornene and related compounds. In addition, we recognized that metalation might provide a convenient preparative route to olefin derivatives whose chemistry could be examined independently. Some results of our studies are described in this and in the following paper.

The Metalation of Norbornene.—Norbornene (1) bears four types of hydrogen atoms, all of which might be considered acidic with respect to a sodium alkyl as a base. However, in view of our introductory discussion, abstraction of a vinyl hydrogen at C-2 would be most favored. The bridgehead protons at C-1 and C-4, although occupying allylic positions, would give rise on removal to an anion for which resonance stabilization would be barred by operation of Bredt's rule.¹⁵ Removal of any of the methylene hydrogens (C-5, C-6, or C-7) would provide a homoallylic anion for which a form of nonclassical resonance stabilization, although conceivable, appears to be unlikely.¹⁶ Rearrangement to the corresponding cyclopropylcarbinyl structure might provide a degree of stabilization by virtue of the electron-withdrawing inductive effect of the cyclopropyl group. Rearrangements of the type shown in Scheme I have been observed with magnesium,¹⁷ lithium,¹⁸ and sodium¹⁹ derivatives of the anion.



That vinyl hydrogen exchange occurred when 1 reacted with butyl- or amylsodium in pentane suspension was demonstrated by carbonation of the reaction mixture and isolation, after acidification, of an acid, m.p. 21.5-22.5°, in good yield which was shown to be norbornene-2-carboxylic acid (2).^{2f} This acid exhibited carbonyl absorption in the infrared at 1678 cm. $^{-1}$ characteristic of an α - β -unsaturated acid.²⁰ The ultraviolet maximum at 229 mµ accords with that expected²¹ for 2 in view of the degree of substitution and strain present in the chromophore. The structure of the acid 2 was proved by catalytic reduction, which afforded the known endo-norbornane-2-carboxylic acid (3), indistinguishable from an authentic specimen.²² Furthermore, an alternate synthesis of 2 was achieved by carbonation of the alkenvllithium reagent obtained after treatment of 2-bromonorbornene (4)²³ in tetrahydrofuran with lithium metal. These transformations are summarized in Scheme II.24,25

Gas chromatographic analysis of the methyl ester failed to reveal the presence of isomers, thus ruling out significant exchange at any position other than C-2. This conclusion was fortified by an experiment in which the metalation mixture was hydrolyzed and the recovered hydrocarbons were analyzed by gas chromatography. The complete absence of nortricyclene indicates that the intermediate illustrated in Scheme I was not formed in detectable amount.

In an attempt to extend the preparative usefulness of the metalation reaction of norbornene, an experi-

- (15) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 298 ff.
- (16) A. Streitweiser, Jr., and R. A. Caldwell, J. Org. Chem., 27, 3360 (1962).

(17) (a) J. D. Roberts, E. R. Trumbell, W. Bennett, and R. Armstrong,
 J. Am. Chem. Soc., 72, 3116 (1950); (b) M. S. Silver, P. R. Shafer, J. E.
 Nordlander, C. Ruckardt, and J. D. Roberts, *ibid.*, 82, 2646 (1960).

(18) (a) G. Wittig and G. Klumpp, Tetrahedron Letters, 10, 607 (1963);
(b) G. Wittig and J. Otten, *ibid.*, 10, 601 (1963); (c) G. Wittig and E. Hahn, Angew. Chem., 72, 781 (1960).

(19) P. K. Freeman, D. E. George, and V. N. M. Rao, J. Org. Chem., 28, 3234 (1963).

(20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules." 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 168.

(21) A. T. Nielsen, J. Org. Chem., 22, 1539 (1957).

(22) J. A. Berson and D. A. Ben-Efraim, J. Am. Chem. Soc., 81, 4083 (1959). We thank Professor Berson for supplying this sample.

(23) N. A. LaBel, *ibid.*, **82**, 623 (1960). We thank Professor LeBel for furnishing a sample of this bromide.

(24) Recently it was reported that acid **2** results when *exo-2*-bromonorbornane-1-carboxylic acid is treated with potassium *t*-butoxide in boiling *t*-butyl alcohol: J. W. Wilt and C. A. Schnieder, *Chem. Ind.*, (London), 951 (1963).

(25) Additional reactions of **2**, **2a**, and **5** will be reported in future papers. R. A. Finnegan and W. H. Mueller, unpublished experiments.

⁽¹³⁾ Unsymmetrical allylic sodium compounds provide predominately the "branched" acid rather than the isomeric "straight-chain" acid on carbonation.^{8,14} In this case the corresponding "straight-chain" acid, 1-cyclohexeneylacetic acid, was not detected.

⁽¹⁴⁾ E. J. Lanpher, Symposia Preprints, Division of Petroleum Chemistry, 136th National Meeting or the American Chemical Society, Vol. 4, No. 4, Atlantic City, N. J., Sept., 1959, p. B5.



Fig. 1.—N.m.r. spectra of norborene-2-carboxylic acid (2, above) and its methyl ester (2a, below).

ment was carried out in which the metalation product, 2-sodionorbornene (5), was treated with excess benzaldehyde instead of carbon dioxide. The product proved to be a mixture from which no pure material could be obtained by repeated fractional distillation. Gas chromatographic analysis indicated the presence of two major products, one of which was identified as benzyl benzoate, whose production from benzaldehyde is apparently a result of the strongly alkaline reaction medium. A small amount of the second product was collected from the gas chromatography column and tentatively identified as phenyl norbornyl ketone (7) on the basis of its microanalysis and infrared and ultraviolet spectra. Its formation probably results from rearrangement of the carbinol (6) formed initially (eq. 8). This product, as well as those formed by the reaction of 5 with benzophene, are currently under investigation.25



The n.m.r. spectra of the acid 2 and its methyl ester (2a) are illustrated in Fig. 1. The vinyl absorption in each case occurs at lower field than in the unsubstituted olefin 1, whose corresponding absorption occurs at τ 4.06.²⁶ These hydrogens are coupled (J = 3 c.p.s.) not

only with the bridgehead proton at C-4,²⁷ but with additional protons as well, since the vinyl doublet appears clearly as a pair of triplets when the scale is expanded ten times, as in the lower spectrum of Fig. 1. This additional coupling is most likely with the exohydrogen at C-6²⁸ and with the other bridgehead proton at C-1²⁹ The bridgehead proton signals may be differentiated by their band shapes. The absorption at τ 6.94 in 2 (τ 7.01 in 2a) is assigned to the proton at C-4 by virtue of its greater apparent degree of splitting. The proximity of the carboxyl functions at C-2 causes a displacement of the C-1 proton signals to slightly lower fields (τ 6.73 and 6.76 in 2 and 2a, respectively). It should be noted that both the bridgehead protons in these compounds are shifted downfield relative to 1 itself, which displays the corresponding signals at r7.22.26 This deshielding of the vinyl and bridgehead protons in 2 and 2a by an electron-withdrawing substituent at C-2 contrasts with the general shielding effect of an electron-donating substituent. In 2-methylnorbornene (5),³⁰ the vinyl signal is shifted upfield to τ 4.58 and the bridgehead protons to 7.24 and 7.46. Furthermore, the positions of the C-1 and C-4 proton resonances are reversed relative to those in 2 and 2a, the signal for the C-1 proton occurring at higher field than that for the C-4 proton as judged by their band shapes (vide supra). These comparisons are summarized in Table 1.

	SCBS11101E	DINORBORN		
	A H	H-4 H-	3	
Compd.	R	H-1	H-3	H-4
1	н	7.22	4.06	7.22
2	$\rm CO_2 H$	6.73	2.93	6.94
2a	$\rm CO_2 CH_3$	6.76	3.11	7.01
5	CH.ª	7 46	4 58	7 29

 $[^]a$ This methyl signal consists of a doublet (J = 2 c.p.s.) centered at $\tau\,8.32.$

⁽²⁶⁾ H. Conroy in "Advances in Organic Chemistry: Methods and Results," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 290.

⁽²⁷⁾ P. Laszlo and P. von R. Schleyer, J. Am. Chem. Soc., 85, 2709 (1963).

⁽²⁸⁾ R. W. King and R. E. Butler, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, p. 84Q.

 ^{(29) (}a) D. J. Collins, J. J. Hobbs, and S. Ternhall, Tetrahedron Letters
 4, 197 (1963); (b) T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, J. Am. Chem. Soc., 85, 1699 (1963).

⁽³⁰⁾ The obtention of **5** is described: R. A. Finnegan and R. S. McNees, J. Org. Chem., **29**, 3241 (1964).

Metalation of endo-5-Hydroxymethylnorbornene.--Treatment of endo-5-hydroxymethylnorbornene ("cyclol," 6) with 2 equiv. of amylsodium, followed by carbonation, led to the isolation of a single crystalline (m.p. 117-117.5°), unsaturated hydroxy acid. The carbonyl absorption in the infrared (1685 cm.⁻¹) and the ultraviolet maximum at 231 m μ both indicated that this acid was α - β -unsaturated. Since the vinylic positions in 6 are nonequivalent, it remained to distinguish between two isomeric possibilities for the derived acid. The acid was assigned structure 7 following the observation that catalytic reduction produced a hydroxy acid which could not be isolated. Instead, there was obtained only a lactone (ν_{max} 1730 cm.⁻¹) whose structure is considered, because of its very easy formation, to be 8, a six-membered lactone, rather than 9, the seven-membered lactone derived from the isomeric acid (Scheme III). The proximity of the functions at the 2- and 6-positions in the intermediate 7a must be responsible for the facile closure to 8.

The n.m.r. spectrum of 7 shows the expected vinyl doublet (J = 3 c.p.s.) at $\tau 2.90$. It may be noted that the protons attached to the carboxyl and hydroxyl groups absorb together as a sharp singlet at $\tau 2.52$. This assignment was verified by conducting a deuterium exchange experiment after which the integral intensity of the $\tau 2.52$ signal was reduced by 84%. In the n.m.r. spectrum of the lactone 8, the methylene group (Scheme III) was evident as a doublet at $\tau 5.58$. The small coupling (J = 1 c.p.s.) observed with the neighboring methine proton at C-6 is consistent with that expected if the six-membered lactone ring occupies a chair conformation. The remaining protons in 8 produce a complex series of signals between τ 7 and 9.

Metalation of Nortricyclene.—An alternate approach to the ion represented in Scheme I would be the abstraction of a hydrogen at C-2 in nortricyclene (10). An attempt to realize this process was made by carrying out the reaction between 10 and amylsodium. When a portion of this reaction mixture was hydrolyzed and the resultant hydrocarbons were analyzed by gas chro-

matography, only nortricyclene was found. Carbonation of the reaction mixture provided an acid in low yield which was easily identified as nortricyclene-1carboxylic acid (11) by mixture melting point and infrared comparisons with an authentic sample.³¹ Further examination of the reaction products was accomplished by diazomethylation of a portion of the crude acids, followed by gas chromatographic analysis of the resultant methyl esters. (A sample of acid 12 and its ester was prepared³² for comparison.) The results of this analysis were consistent with the observation that acid 11 was obtained exclusively since no isomeric esters were detected. These results point to abstraction of a cyclopropyl (C-1) hydrogen in the metalation step and are summarized in Scheme IV. The acidity of cyclopropyl hydrogens may be explained by the increase in the s character of the C-H bond orbitals which results when the normally tetrahedral carbon atom is contained in a small, strained ring.^{33,34} The acidity of cyclopropane itself was demonstrated several years ago by its metalation with amylsodium.³⁵ More recently, the even greater acidity of some highly strained [1.1.0]bicvclobutane derivatives has been reported.³⁶ The enhanced lability of cyclopropenyl hydrogens toward bases appears to have a similar origin.³⁷

The n.m.r. spectrum of acid 11 was determined and the assignments are listed in Table 2 along with those of the parent hydrocarbon 10. The assignment of protons in 10 follows from the relative integration

(31) H. Hart and R. A. Martin, J. Org. Chem.. 24, 1267 (1961). We thank Professor Hart for providing this comparison sample

(32) Prepared by Mr. A. W. Hagen by the method of Roberts and coworkers.^{17a}

(33) The exo orbitals in cyclopropane are calculated to be sp^{2.28} hybrids: L. J. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 11, p. 518.

(34) C. S. Foote, *Tetrahedron Letters*, 9, 579 (1963).
(35) E. J. Lanpher, L. M. Redman, and A. A. Morton, *J. Org. Chem.*

23, 1370 (1958).
 (36) (a) J. Meinwald, C. Swithenbank, and A. Lewis, J. Am. Chem.

Soc., 85, 1880 (1963); (b) G. L. Closs and L. E. Closs, *ibid.*, 85, 2022 (1963).
 (37) (a) K. B. Wiberg, R. K. Barnes, and J. Albin, *ibid.*, 79, 4994 (1957);

(b) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6379 (1960).

Fig. 2.-N.m.r. spectrum of the dimethyl ester of Thiele's acid.

values of 3:6:1 observed for the three signals in the spectrum. The chemical shifts are in close agreement with those reported by Srinivasan³⁸ for 10; however, we observe the signal due to the six methylene hydrogens as a doublet (J = 1.4 c.p.s.) rather than a singlet.³⁸ This coupling is most likely with the lone bridgehead hydrogen since the latter appears as a broad multiplet whereas the cyclopropyl hydrogens appear as a sharp singlet. Scale expansion (ten times) of the methylene doublet gave evidence of additional small splitting in each member of the doublet.

In acid 11, the carboxyl group causes a downfield shift of all the remaining hydrogens. Particularly affected are the adjacent methylene protons which are assigned to a doublet at τ 8.54 (J = 1.5 c.p.s.) and the remaining cyclopropyl hydrogens, assigned to another peak (weight of two hydrogens) at τ 8.10. This latter peak shows very small splitting which gives it the appearance of a triplet. The shift of this pair of protons by nearly a τ -unit from their position in the unsubstituted hydrocarbon is paralleled by the shift of the *cis* hydrogens in cyclopropanecarboxylic acid³⁹ relative to cyclopropane⁴⁰ itself.

The spectrum of acid 12 was also determined and the proton α to the carboxyl at C-2 was assigned to a triplet (J = 1.2 c.p.s.) at τ 7.62. The lone bridgehead proton appeared as a broad singlet at τ 7.76. The remainder of the spectrum was complicated by the lack of symmetry in the molecule. A substituent on one bridge of the norticyclene skeleton causes the methylene hydrogens of an adjoining bridge to become nonequivalent, and thus to exhibit an AB spectrum. What is very likely half of an AB quartet was observed in the spectrum of 12 centered at τ 8.40 (J = 11.5 c.p.s.).⁴¹ This effect is most lucidly seen in the spectrum of the symmetrical hydrocarbon, tricyclene (13). A sharp singlet at τ 9.18 (weight of nine hydrogens) is evidently due to

⁽³⁸⁾ R. Srinivasan, J. Am. Chem. Soc., 83, 4923 (1961).

(39) K. B. Wiberg and B. J. Nist, ibid., 85, 2788 (1963).

(40) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Ltd., London, 1959, p. 52.

(41) Additional complication in the spectrum of **12** may stem from the nonequivalence of the cyclopropyl hydrogens.

the three methyl groups in 13. Another sharp singlet (weight of two hydrogens), observed at τ 8.99, can be assigned to the two cyclopropyl hydrogens, while a broad singlet at τ 8.61 is assigned to the lone bridgehead hydrogen. As expected, this latter signal is shifted upfield relative to its position in nortricyclene (10). The remaining four protons in 13 give rise to an AB quartet ($J_{AB} = 10.5$ c.p.s., integrated intensity ratio 8.5:13:15:9.0) with one pair of lines centered at τ 8.34 and the other at 8.97. (Each line is somewhat broadened by further coupling.) The upfield signals are tentatively assigned to the pair of hydrogens proximate to the methyl groups (B in 13), while the downfield lines stem from the pair A. An analogous set of shifts has been observed in the spectrum of [2.1.1] bicyclohexane by Srinivasan.38

Metalation of Norbornadiene .-- The treatment of norbornadiene (14) with amylsodium provided, after carbonation, a 49% yield (see Experimental) of a crystalline acid for which the empirical formula $C_6H_6O_2$ was indicated by microanalytical data and the equivalent weight. The infrared $(\nu_{max}^{KBr} 1675 \text{ cm}.^{-1})$ and ultraviolet $[\lambda_{\max}^{95\% \text{ EtoH}} 222 \text{ m}\mu (\log \epsilon 4.23)]$ spectra indicated an α,β -unsaturated acid and its high melting point (204-205° subl.) suggested that it was a dibasic acid, $C_{12}H_{12}O_4$. The relationship of this molecular formula to that of the starting material became apparent when the product was recognized as Thiele's acid,⁴² a known dimer of cyclopentadienecarboxylic acid. This acid has been assigned structure 15 by Peters on the basis of a series of chemical and spectroscopic investigations.⁴³ The acid 15 is the major product obtained when cyclopentadienyl Grignard reagent^{43a} or the corresponding sodium^{43c,44} or potassium⁴² reagent is carbonated, and the resultant carboxylate salt is acidified. Positive identification of the metalation product as 15 was achieved by comparison (mixture melting point undepressed, infrared, and ultraviolet spectra) with an authentic sample prepared from cyclopentadienylmagnesium bromide (Scheme V). In addition, the dimethyl esters,^{43a} m.p. 84-84.5°, prepared from each of the acid samples were shown to be identical by the usual criteria.^{2d} As an adjunct to the demonstration⁴³ of structure 15 for Thiele's acid, the n.m.r. spectrum of its dimethyl ester was determined. This spectrum is reproduced in Fig. 2 along with proton assignments which are in agreement with the structural conclusions of Peters.

(42) J. Thiele, Ber., 34, 68 (1901).

(43) (a) D. Peters, J. Chem. Soc., 1761 (1959); (b) ibid., 1832 (1960); (c) ibid., 1042 (1961).

(44) K. Ziegler, H. Froitzheim-Kuhlhorn, and K. Hafner, Chem. Ber., 89, 434 (1956).

The genesis of 15 from 14 most likely involves the initial abstraction of a vinyl hydrogen^{2d,45} followed by either concerted or stepwise production of cyclopentadiene and acetylene. Carbonation would give largely sodium cyclopentadienecarboxylate, which on acidification yields 15 (Scheme VI). Acetylene and cyclopentadiene were detected gas chromatographically when a portion of the reaction mixture was hydrolyzed instead of carbonated. The equilibrium of cyclopentadiene and sodium acetylide with cyclopentadienylsodium and acetylene should lie well to the right, as shown in Scheme VI, in view of the greater acidity of cyclopentadiene relative to acetylene.⁴⁶ This helps to account for our inability to detect propiolic acid in the reaction mixture. Products derived by carbonation of intermediate 16 also escaped isolation, although similar intermediates have been reported in certain nortricyclene fragmentations.^{18a, 19, 47} This ionic cleavage of norbornadiene to cyclopentadiene and acetylene, formally a reverse Diels-Alder reaction, has its counterpart in the thermal^{48,49} and photolytic⁵⁰ decomposition of the diene.

Finally, the contrasting behavior of butyllithium towards 14 should be noted. Although butyllithium is known to exchange the vinyl hydrogens of norbornadiene, ^{16,51} the predominant mode of reaction appears to be addition¹⁸ of the lithium alkyl to the diene. These results are illustrative of what seems to be a very general⁵² reactivity relationship; *i.e.*, when a substrate offers the possibility of both addition and abstraction reactions, the lithium reagent will tend to add preferentially, while the sodium reagent will tend to abstract hydrogen preferentially.

Experimental

The infrared spectra were taken on the Infracord Model 137B, the Baird Model B, or the Perkin-Elmer Model 21 spectrophotometers. The Cary Model 10 and the Perkin-Elmer 202 were used to take ultraviolet spectra. N.m.r. spectra were run on the Varian Associates A-60 n.m.r. spectrometer. Analyses were performed by Dr. A. Bernhardt, Mülheim, Germany. Unless otherwise noted, the melting points were taken on a Fisher-Johns melting point block and are uncorrected. The boiling points are uncorrected. Gas chromatography was done with a Wilkins Aerograph gas chromatograph, with helium as the carrier gas and with a 5-ft. (20% SF-96 silicone grease on firebrick) column, unless otherwise noted.

Metalation of Norbornene.—To a suspension of 0.135 mole of butylsodium-sodium chloride^{53,54} in pentane was added 0.15 mole (14 g.) or norbornene (1) and the mixture was sealed under a nitrogen atmosphere. It was shaken occasionally and, after 17 days, was carbonated with an excess of solid carbon dioxide. The carbonation product was hydrolyzed, filtered, and extracted four times with a total of 150 ml. of ether. The aqueous layer was acidified (concentrated HCl), extracted twice with a total of 275 ml. of ether, saturated with sodium chloride, and extracted again with a total of 450 ml. of ether. The ether extracts were dried over calcium sulfate, filtered, and evaporated to leave 17.81 g. of crude product. This was fractionated to give 11.16 g. of 2-norbornene-2-carboxylic acid (2, 60% yield based on 0.135 mole of amylsodium): m.p. 21.5–22.5° (water bath), b.p. 96° at 0.6 mm., ν_{max}^{Bim} 1678,1595 cm.⁻¹, λ_{max}^{Bim} 229 mµ (log ϵ 3.85). Anal. Calcd. for CsH₁₀O₂: C, 69.54; H, 7.30. Found: C, 69.27; H, 7.38.

From a metalation of 0.10 mole of 1 with *n*-amylsodium for 81 days, 2 was obtained in 51.5% yield. Gas chromatographic analysis of a hydrolyzed aliquot from a 2-day-old mixture of amylsodium and norbornene in pentane showed that nortricyclene was not present; it was also absent in hydrolyzed aliquots taken after a longer time. The gas chromatography was done with a 10-ft. dimethyl sulfolane column at 47° with a helium flow rate of 42 cc./min.

Methyl 2-Norbornene-2-carboxylate (2a).—A solution of 12.13 g. of the crude acid was refluxed for 48 hr. in methanol (125 ml.) containing several drops of sulfuric acid. The solution was poured in 500 ml. of cold water and extracted with ether. The combined ether extracts were washed with dilute potassium hydroxide solution and with water. Drying the ether solution and evaporation of the solvent left 7.29 g. of crude ester. This was fractionated to give 5.46 g. of 2a, b.p. 70° at 4 mm., ν_{max}^{film} 1709 and 1595 cm.⁻¹, shown to be pure by gas chromatographic analysis (diethylene glycol succinate column, 170°, 44 cc./min.). The ester was also prepared by diazomethylation of the acid.

Anal. Caled. for C₉H₁₂O₂: C, 71.02; H, 7.95. Found: C, 70.85; H, 8.04.

2-Norbornene-2-carboxamide and Carboxanilide.—A 1.08-g. sample of 2 was refluxed with 6 ml. of thionyl chloride for 1.25 hr. The thionyl chloride was then distilled, the acyl chloride was allowed to cool, and about one-half of it was added dropwise with swirling to 100 ml. of concentrated ammonium hydroxide; the rest was added to 7 ml. of aniline dissolved in 100 ml. of ether. The amide-ammonium hydroxide mixture was extracted with 40 ml. of ether and was then extracted three times with a total of 175 ml. of chloroform. The combined extracts were dried over magnesium sulfate, filtered, and evaporated to leave 0.52 g. of crude amide. The amide was purified by subliming (90° at 0.5 mm.) it twice: m.p. 142.7–144.6° (cor., sealed tube, subl.), $\rho_{\rm max}^{\rm MB}$ 1678 (carbonyl) and 1629–1642 cm.⁻¹ (amide II), $\lambda_{\rm max}^{\rm MB}$ 222 m μ (log ϵ 3.75).

Anal. Calcd. for $C_8H_{11}NO$: N, 10.21. Found: N, 10.17. The aniline reaction mixture was washed with 25% aqueous hydrochloric acid and was dried (MgSO₄), filtered, and evaporated to leave 0.64 g. of the crude anilide. This was dissolved in benzene, put on a Merck acid-washed alumina column (15 cm. long, 1.5 cm. in diameter) packed in benzene, and eluted with benzene. The anilide, purified by chromatography, was twice recrystallized from ligroin-chloroform and was vacuum dried, m.p. 157.5–159.0°.

Anal. Calcd. for C14H16NO: N, 6.57. Found: N, 6.31.

Hydrogenation of 2-Norbornene-2-carboxylic Acid (2). Preparation of endo-Norbornane-2-carboxylic Acid (3).—A solution

⁽⁴⁵⁾ Our results, however, do not rule out the possibility that the cleavage is initiated by loss of a proton from C-7.

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⁽⁵³⁾ Butyl- and amylsodium suspensions were prepared by the method of Morton and co-workers.⁵⁴ The metal alkyl content was determined by carbonation of an aliquot of the (well-shaken) suspensions and titration of the ether extracted acids.

⁽⁵⁴⁾ A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, J. Am. Chem. Soc., 72, 3785 (1950).

of 1.68 g. of 2 in glacial acetic acid was treated with hydrogen over 50 mg. of 10% palladium on carbon as a catalyst (magnetic stirring) until no more hydrogen was taken up. The crystalline acid, left after filtration and evaporation of the solvent, was thrice distilled to give 1.32 g. of *endo*-norbornane-2-carboxylic acid (3) melting at 61.5-62.5°. Part of this was recrystallized from acetonitrile, m.p. 64.5-66.5°. A mixture melting point of this acid with an authentic sample of *endo*-norbornane-2-carboxylic acid,²² m.p.65.0-6 6.5°, was undepressed (65.0-66.0°). The infrared spectra of the two specimens were indistinguishable.

Preparation of 2-Norbornene-2-carboxylic Acid (2) from 2-Bromonorbornene (4).—2-Bromonorbornene²³ (1.0 g., 0.00546 mole) was dissolved in 30 ml. of tetrahydrofuran which had been purified by passage through alumina of activity I. Over a period of 45 min., 0.3 g. (0.043 g.-atom) of lithium metal, chopped in small pieces, was added. The mixture was stirred and refluxed for 45 min. and then poured over solid carbon dioxide. The carbonation product was dissolved in water and extracted with ether. The aqueous layer was acidified (concentrated HCl), extracted twice with a total of 75 ml. of ether, saturated with sodium chloride, and extracted four times with a total of 75 ml. of ether. The combined ether extracts were dried (CaSO₄), filtered, and evaporated to leave 0.46 g. of acid identical with 2 as shown by the infrared spectrum.

Metalation of endo-5-Hydroxymethylnorbornene (6).-To 0.202 mole of amylsodium-sodium chloride in pentane was slowly added 12.524 g. (0.101 mole) of endo-5-hydroxymethylnorbornene (6) and exo-5-hydroxymethylnorbornene (80% endo isomer). The container was sealed under helium and shaken occasionally. After 34 days at room temperature the mixture was carbonated with excess solid carbon dioxide. The carbonation product was hydrolyzed and the solution was filtered. The alkaline solution was extracted three times with 150-ml. portions of ether. The combined ether extracts were dried (CaSO₄), filtered, and evaporated to leave 6.75 g. of liquid containing 78% starting material, shown by gas chromatographic analysis (172°, 46 cc./min.). The aqueous layer was made acid (dilute H_2SO_4) and was twice extracted with 200-ml. portions of ether. It was then saturated with sodium chloride and extracted six times with 200-ml. portions of ether. The combined ether extracts were dried (CaSO₄), filtered, and evaporated to leave 10.228 g. of yellow oil. Some crystals formed in the liquid after a period of refrigeration and were removed for use as seed crystals. The crude acid was dissolved in ether and was filtered to remove 0.682 g. of apparently polymeric material which did not melt below 300°. The filtrate was evaporated to small volume, cooled, and seeded. White, crystalline endo-6-hydroxymethyl-2-norbornene-2-carboxylic acid (7, 1.516 g., 15.3% yield based on unrecovered starting material), melting at 112-115°, was formed in the solution. Recrystallization from ether-petroleum ether (b.p. 65-110°) raised the meiting point to 115-116°. An analytical sample was prepared by sublimation (60° at 0.05 mm.): m.p. 117.0-117.5°, ν_{\max}^{KB} 1685 cm.⁻¹, $\lambda_{\max}^{95\%}$ EtoH 231 m μ (log ϵ 3.86).

Anal. Calcd. for C₉H₁₂O₃: C, 64.27; H, 7.19; neut. equiv., 168. Found: C, 64.44; H, 6.94; neut. equiv., 168.

The mother liquor was distilled at 0.05 mm. and 120° . The distillate (0.790 g.) was identified as caproic acid by its infrared spectrum. The residue was nonvolatile and apparently polymeric.

Hydrogenation of endo-6-Hydroxymethyl-2-norbornene-2-carboxylic Acid (7). Formation of the Lactone (8) of cis-endo-6-Hydroxymethylnorbornane-2-carboxylic Acid (7a).—An absolute ethanol suspension of 20 mg. of 5% palladium-on-carbon catalyst was reduced (magnetic stirring). A 148-mg. sample of the acid (7) was dissolved in absolute ethanol and added to the catalyst. The sample of 7 took up 1.12 equiv. of hydrogen. The catalyst was filtered off and the solvent was evaporated to leave 135 mg. of the lactone 8. The lactone was dissolved in ether, washed with aqueous sodium bicarbonate, and dried (Ca-SO₄). The solution was filtered and the solvent was evaporated. When heated, a sublimed (50° at 10 mm.) sample turned from white to clear and melted at 120-125°.

Anal. Caled. for $C_9H_{12}O_2\colon$ C, 71.02; H, 7.95. Found: C, 71.43; H, 8.25.

Partial Deuteration of 6-Hydroxymethyl-2-norbornene-2-carboxylic Acid (7).—A 0.100-g. sample of 7 was dissolved in 3 ml. of acetone, and 2 ml. of deuterium oxide (99.5%) was added. After 15 min. the solution was evaporated to leave 0.095 g. of crystalline material. This procedure was repeated, to give 0.087 g. of crystals, m.p. $112.5-114.5^{\circ}$. The infrared spectrum showed that it was partially deuterated. See discussion of the n.m.r. spectrum in the text.

Metalation of Nortricyclene (10).-To a suspension of amylsodium-sodium chloride (0.095 mole) in pentane (200 ml.) was added 8.9 g. (0.095 mole) of nortricyclene. The mixture was sealed under an inert atmosphere and allowed to stand with occasional shaking for 22 days at room temperature. At the end of this time a small aliquot (10 ml.) of the suspension was hydrolyzed with ice and extracted with pentane. This pentane extract, after being dried, was analyzed by gas chromatography (dimethyl sulfolane column) and found to contain only nortricyclene. The remainder of the reaction mixture was then treated with a large excess of solid carbon dioxide and the resultant carboylic acids (4.54 g.) were isolated in the usual way after acidification and ether extraction. A portion of the crude acid mixture was analyzed after diazomethylation by gas chromatography. No isomeric carboxylic esters were detected by this method. The remainder of the acid mixture was divided into a soluble, crystalline portion (1.48 g.) and an insoluble dark-colored, resinous portion (2.7 g.) by digestion with Skellysolve B. The insoluble portion was chromatographed on silica gel to provide an additional 0.40 g. of the crystalline acid along with a number of uncharacterizable oils. The combined crystalline products were recrystallized three times from Skellysolve B and sublimed (0.1 mm., room temperature) to give 0.58 g. (5%) of nortricyclene-1-carboxylic acid (11), m.p. $119-121^{\circ}$ alone or admixed with an authentic sample.^{a1} The infrared spectra (KBr) of the two samples were indistinguishable.

A similar metalation mixture of nortricyclene and amylsodium which was allowed to react for 6 months provided, after carbonation, an 18% yield of once-sublimed 11, m.p. 114-118°.

Reaction of Norbornadiene (14) with Amylsodium.—To a Morton flask containing 0.145 mole of amylsodium-sodium chloride in pentane was added 18.4 g. (0.20 mole) of norbornadiene (14), all at one time, with high-speed stirring, under a helium atmosphere. The reaction mixture was stirred at high speed and at room temperature for 5 hr. and was then carbonated with an excess of solid carbon dioxide. The carbonated product was hydrolyzed and worked up in the manner previously described to provide 17.75 g. of crude acid mixture. This mixture was diluted with petroleum ether and cooled. In three separate crops, a total of 6.298 g. of crude, crystalline dicyclopentadienedicarboxylic acid was obtained. Part of the product was twice recrystallized from methanol and was further purified by sublimation (90° at 0.025 mm.), giving a white powder (15): m.p. 204-205° (cor., sealed tube, subl.), lit.⁴³⁰ m.p. 201°, ν_{max}^{857} 1675 cm. -1, λ_{max}^{8650} H222 m μ (log ϵ 4.23).

Anal. Calcd. for C₁₂H₁₂O₄: C, 65.45; H, 5.55; neut. equiv., 110. Found: C, 65.25; H, 5.72; neut. equiv., 109.

When the residue, remaining after removal of the crude acid described above, was submitted to vacuum distillation, 3.409 g. (0.029 equiv.) of caproic acid was obtained. Although a small additional amount of Thiele's acid sublimed from this tarry residue, it was not further examined except for infrared analysis which did not reveal the presence of acetylenic absorption. The yield of crude Thiele's acid was calculated to be 49% based on the available amylsodium (*i.e.*, taking into account the amount of caproic acid formed) and assuming a stoichiometry of one amylsodium to one norbornadiene.

Preparation of Thiele's Acid.48-In a 250-ml., round-bottomed flask equipped with stirrer, dropping funnel, and condenser was put 0.3 mole of methylmagnesium bromide in ether and to this was added in several portions, with stirring, 18.4 g. (0.29 mole) of cyclopentadiene monomer (b.p. 39.5-42.5°) obtained by distilling dicyclopentadiene through a column filled with glass helices. The solution was refluxed for 26 hr., and the contents of the flask were poured onto solid carbon dioxide. Water was later added and the solution was acidified (dilute H₂SO₄); material precipitated and was filtered off. The aqueous layer was extracted seven times with a total of 400 ml. of ether. The precipitate was dissolved in ammonium hydroxide and the solution was filtered. Upon acidification (dilute H_2SO_4) the acid was reprecipitated; it was dissolved in absolute methanol, treated with activated charcoal, and filtered through Celite. The solution was evaporated to small volume and seeded with the original precipitate. White crystals were formed, m.p. 202-205° (cor., sealed tube, subl.), lit.43c m.p. 201°. The infrared spectrum of this acid was indistinguishable from that of the acid 15 obtained from the metalation of 14. The mixture melting point $(202-205^{\circ}, \text{ cor.}, \text{ sealed tube, subl.})$ was undepressed. More of the acid was obtained from the ether extracts.

The methyl ester prepared from this acid (methanol and sulfuric acid) had m.p. $84-84.5^{\circ}$ after recrystallization from petroleum ether (lit.^{43a} m.p. 85°). The melting point of this material was undepressed ($84-84.5^{\circ}$) when mixed with a sample of the ester, m.p. $83.5-84^{\circ}$, similarly obtained from 15. The infrared spectra of the two ester samples were indistinguishable.

Formation of Acetylene in the Cleavage Reaction of Norbornadiene.—In order to demonstrate that acetylene is formed in the norbornadiene-amylsodium reaction a series of hydrolyses was carried out. To 0.154 mole of amylsodium-sodium chloride suspended in pentane was added 14.72 g. (0.16 mole) of norbornadiene; the bottle was sealed under helium. After 4 hr. the bottle was thoroughly shaken and a 4-ml. aliquot was transferred by pipet to a tube having a sidearm and ball joint and having an opening for a serum cap. The suspension was evaporated to dryness under vacuum. The tube was chilled in ice-water, helium was admitted, and water was injected through the serum cap. The gas liberated was analyzed by gas chromatography (dimethyl sulfolane column, 11° , 47.5 cc./at min.); pentane, acetylene, and cyclopentadiene were present in the gas. The ratio of the pentane peak to that of the acetylene peak was 4:1. After 24 hr. another aliquot was hydrolyzed; the pentane-acetylene ratio was 0.33:1. A third aliquot, taken and hydrolyzed 4 days after the beginning of the reaction, generated no pentane.

Organometallic Chemistry. VIII. The Metalation of Camphene, Norcamphene, and α -Pinene^{1,2}

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Sodio derivatives of camphene, norcamphene, and α -pinene have been prepared by treatment of the olefins with amylsodium. From the corresponding organometallic intermediates, the following carboxylic acids were formed by carbonation: from camphene, 3,3-dimethyl-2-norbornylideneacetic acid; from norcamphene, exo-3-methylene-2-norbornanecarboxylic acid and 2-norbornylideneacetic acid; and from α -pinene, mertenylcarboxylic acid and endo-2(10)-pinene-3-carboxylic acid. Some chemical and spectroscopic properties of these products are presented and discussed.

The subject of olefin metalation was outlined briefly in our preceeding article² with particular reference to antecedent work done with cyclic olefins. The application of the metalation reaction to the strained bicyclic olefins norbornene, cyclol, and norbornadiene, as well as to the cyclopropane analog nortricyclene, was described.² Some of the results are summarized in eq. 1-4. In each case the metalation products were char-

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acterized by carbonation followed by isolation and proof of structure of the resultant carboxylic acids. Norbornene (eq. 1) provided a good yield of norbornene-2carboxylic acid via the intermediate 2-sodionorbornene.⁵ In similar fashion, cyclol provided the corresponding unsaturated acid (eq. 2). Norbornadiene (eq. 3) provided Thiele's acid in nearly quantitative yield. This product ensues from a novel cleavage reaction of the starting diene which probably is initiated by metalation at a vinyl position. Finally, nortricyclene provided an acid derived by metalation at the 1-position (eq. 4).

We have extended application of the metalationcarbonation sequence to camphene and norcamphene, in which the double bond is exocyclic to one of the rings, as well as to α -pinene, in which the double bond is trisubstituted. The present article describes these additional results.

Metalation of Camphene.—Since the allylic hydrogen in camphene (1) is tertiary and occupies a brideghead position, exchange of a terminal vinyl hydrogen is the predicted reaction course when camphene reacts with amylsodium. In accord with this view, carbonation of such a reaction mixture led to the production in fair yield of an acid, m.p. 129.5–130.0°, characterized as 3,3-

(5) Reactions of 2-sodionorbornene with carbonyl compounds other than carbon dioxide are under investigation. R. A. Finnegan and W. H. Mueller, experiments to be published.

⁽²⁾ Paper VII: R. A. Finnegan and R. S. McNees, J. Org. Chem., 29, 3234 (1964).

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⁽⁴⁾ Frederick Gardner Cottrell Fellow, 1960-1961, 1962-1963; National Science Foundation Cooperative Fellow, 1961-1962; Petroleum Research Fund Fellow, 1963. Portions of this paper have been adapted from a thesis presented by R. S. M. to the Department of Chemistry, Ohio State University, winter, 1963, in partial fulfillment of the requirements for the M.S. degree.