obtained from the metalation of **14**. The mixture melting point (202–205°, cor., 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° after recrystallization from petroleum ether (lit.[43a] m.p. 85°). The melting point of this material was undepressed (84–84.5°) when mixed with a sample of the ester, m.p. 83.5–84°, 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]

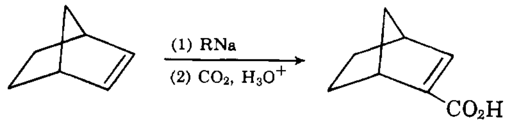
Richard A. Finnegan[3] and Robert S. McNees[4]

Department of Medicinal Chemistry, School of Pharmacy, State University of New York at Buffalo, Buffalo 14, New York, and the Department of Chemistry, The Ohio State University, Columbus 10, Ohio

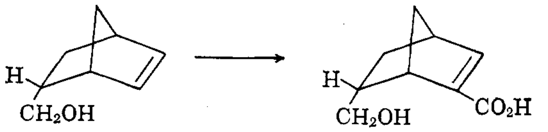
Received July 10, 1964

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.

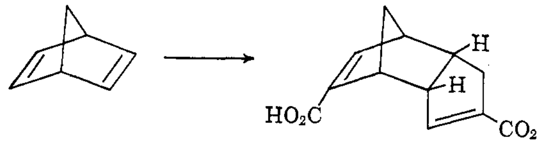
The subject of olefin metalation was outlined briefly in our preceeding article[2] with particular reference to antecedent work done with cyclic olefins. The application of the metalation reaction to the strained bicyclic olefins norbornene, cyclol, and norbornadiene, as well as to the cyclopropane analog nortricyclene, was described.[2] Some of the results are summarized in eq. 1–4. In each case the metalation products were characterized by carbonation followed by isolation and proof of structure of the resultant carboxylic acids. Norbornene (eq. 1) provided a good yield of norbornene-2-carboxylic 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).



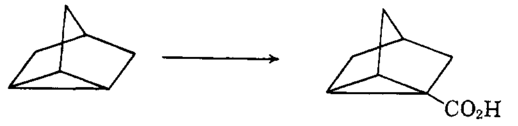
(1)



(2)



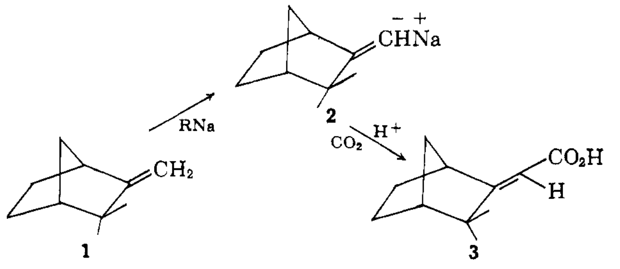
(3)



(4)

We have extended application of the metalation–carbonation 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 bridgehead 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-



---

[1] This research was generously supported by grants from the Research Corporation and the Petroleum Research Fund of the American Chemical Society.

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

[3] Author to whom inquiries may be sent at the Buffalo address.

[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.

[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.

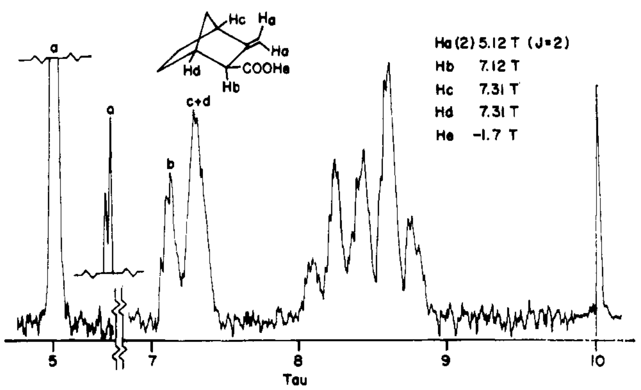
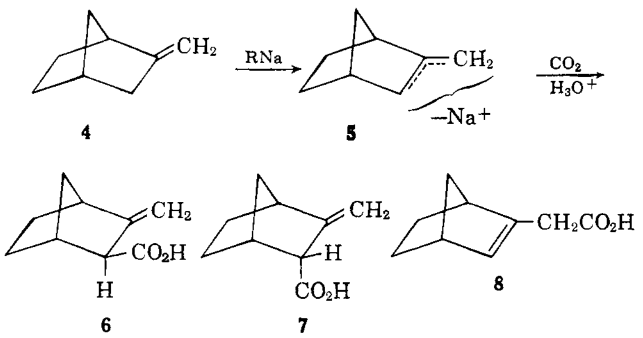
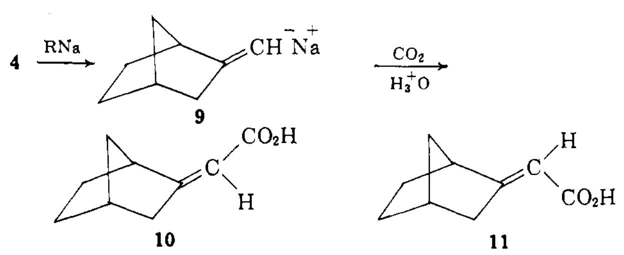


Fig. 1.—N.m.r. spectrum of *exo*-3-methylene-2-norbornanecarboxylic acid (6).

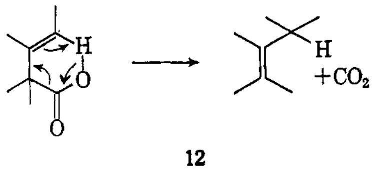
dimethyl-2-norbornyldieneacetic acid (**3**, carboxyl *cis* to the bridgehead). Structure **3** was consistent with the microanalytical data obtained for this acid. In addition, it exhibited absorption in the infrared at 1690 cm.$^{-1}$ (KBr) and in the ultraviolet (95% ethanol) at 227 mμ (log ϵ 4.17) as anticipated for the conjugated carboxyl group. The integrated n.m.r. spectrum of **3** provided detailed verification of its structure. In addition to the carboxyl proton signal at τ -2.31, the spectrum showed absorption for a lone hydrogen in the olefinic region at τ 4.62 (singlet), a broad multiplet at τ 6.00 (weight of one hydrogen) arising from the allylic bridgehead proton, and a sharp singlet (weight of six hydrogens) at τ 8.91 due to the geminal methyl groups. The fact that the methyl resonance occurs at virtually the same field in the acid **3** as it does in the hydrocarbon **1** (τ 8.99[6]) can be taken as definitive evidence for the geometry of the double bond as shown in **3**. A model of the isomer in which the carboxyl group is *cis* to the methyl groups illustrates considerable steric interaction, which would be expected almost certainly to alter the magnetic environment of the methyl protons. This stereochemical conclusion also accords with the expectation that carbonation of the sodio intermediate (**2**) would occur to give the least hindered acid. Both the metalation step and the carbonation step would be subject to strong steric influence, especially if they are assumed to be heterogeneous reactions occurring at phase boundaries; therefore, no conclusion can be made regarding the geometric stability of the intermediate vinyl sodium compound (**2**). Although acid **3** has been mentioned in the literature,[7,8] the geometry of the double bond has not previously been defined. It seems pertinent to suggest that both previous preparations[7,8] of **2** can be rationalized to fit the present geometrical assignment.



Metalation of Norcamphene.—The available allylic hydrogens in addition to the terminal vinyl hydrogens in the norcamphene molecule **4** offer a number of possibilities for the formation of isomeric acids in the metalation–carbonation sequence. Production of the allylic ion **5** could lead to the three acids, **6**, **7**, and **8**, on carbonation. Also likely in view of the recent studies of Broaddus[9] is the formation of the vinylsodium intermediate (**9**), which could lead to isomers **10** and **11** on carbonation. In the event, treatment of **4** with an equimolar amount of amylsodium in pentane suspension followed by carbonation provided a mixture of acids which could be separated by fractional distillation into a major product (29% yield) and a minor product (5% yield). The major product (b.p. 97–98° at 0.25 mm.) crystallized and could be further purified by recrystallization from petroleum ether (b.p. 65–110°). The analytically pure sample had m.p. 61.0–61.5°. The infrared spectrum showed carbonyl absorption at 1705 cm.$^{-1}$, typical for a nonconjugated acid and consistent with the absence of an ultraviolet maximum above 200 mμ. Furthermore, infrared maxima at 1660 and 895 cm.$^{-1}$, ascribed to the presence of an exocyclic methylene group, limits the structural possibilities for this acid to **6** or **7**. This conclusion is supported by vinyl hydrogen absorption corresponding to two such protons in the n.m.r. spectrum of this acid (Fig. 1). The *exo* configuration is assigned to the carboxyl groups (structure **6**) on the grounds that approach of a reagent to the norbornane skeleton is greatly facilitated on the *exo* side[10]; hence, carbon dioxide should react with ion **5** to give **6**.



The structure and stereochemistry of **6** were proved by a combination of two chemical transformations. The pyrolysis of β,γ-unsaturated acids has been shown by Arnold[11] to proceed by migration of the double bond concerted with the loss of carbon dioxide, as in **12**.



Accordingly, pyrolysis of acid **6** led to an olefin identified as 2-methylnorbornene (**13**) by its n.m.r. spectrum.[12]

---

(6) 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. 287.

(7) W. Treibs and H. Ortmann, *Chem. Ber.*, **93**, 545 (1960).

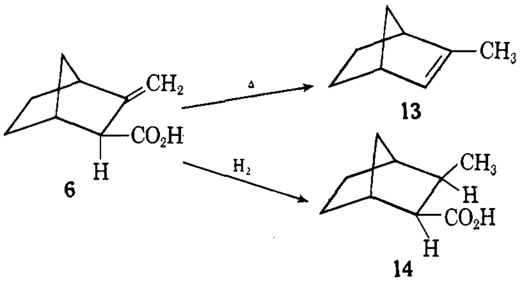
(8) M. G. Langlois, *Ann. chim.* (Paris), [**9**] **12**, 265 (1920).

(9) C. D. Broaddus, T. J. Logan, and T. J. Flautt, *J. Org. Chem.*, **28**, 1174 (1963).

(10) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 303.

(11) R. T. Arnold and M. J. Danzig, *J. Am. Chem. Soc.*, **79**, 892 (1957).

(12) The n.m.r. spectrum of **13** was discussed in ref. 2.

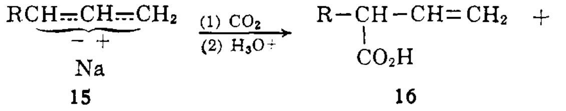


6 13 14

Furthermore, catalytic reduction of 6 provided the known[13] *exo-cis*-3-methylnorbornane-2-carboxylic acid, **14**, whose n.m.r. spectrum is reproduced in Fig. 2.[14] The presence of the *exo*-carboxyl group in 6 offers steric interference sufficient to cause reduction of the double bond to proceed from the *endo* face of the molecule.

As mentioned above, acid 6 was accompanied by a minor isomer which was separable by fractional distillation. The distilled material crystallized and had m.p. 116.5–117.0° after being recrystallized several times from petroleum ether. This acid, in contrast to 6, was α,β-unsaturated as judged by the carbonyl absorption at 1680 cm.$^{-1}$ and the ultraviolet maximum (95% ethanol) at 228 mμ (log ϵ 4.05). Study of a model of ion 9 (the presumed precursor of the conjugated acid, *vide infra*) did not permit a clear choice concerning the steric factors which would be expected to determine the geometry of the derived acid. The choice between structures 10 and 11, however, was eventually made in favor of 10 after examination of the n.m.r. spectrum of this acid. This spectrum shows, in addition to the acidic proton at τ −2.25 and the single vinyl proton at 4.49 (broad singlet), a signal (weight of one proton, broad singlet) at 6.01. This latter signal arises from the allylic bridgehead proton at C-1 and its marked downfield shift[15] must be due to the proximity of the *cis*-oriented carboxyl group. This conclusion is evident from the fact that the shift for the C-1 proton in 10 is exactly the same as that for the corresponding C-1 proton in acid 3, in which the geometry of the double bond is secured on other grounds (*vide supra*).

The observation that 6 rather than 8 was obtained after carbonation of the allylic ion 5 accords with previous reports[9,16] of the distribution of products derived from unsymmetrically substituted allylsodium derivatives. In the case of acyclic ions such as 15, a mixture of branched (16) and straight-chain (17) acids is usually obtained on carbonation. The branched-chain isomer invariably predominates. In the present example, the "branched-chain" isomer 6 was isolated exclusively.[17] This result has a very close analog in the report[18] that acid 19 was the sole olefinic acid isolated after carbonation of ion 18.



$$\underbrace{RCH{=}CH{=}CH_2}_{-\ \ +}\atop Na \xrightarrow[(2)\ H_3O^+]{(1)\ CO_2} R-\underset{\displaystyle CO_2H}{\underset{|}{CH}}-CH=CH_2 \;+\; RCH=CH-CH_2CO_2H$$

15 16 17

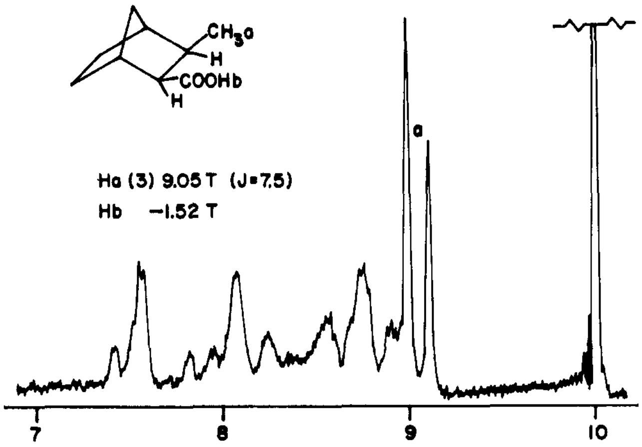
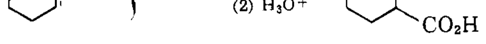
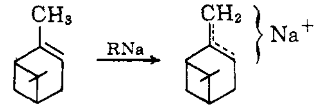


Fig. 2.—N.m.r. spectrum of *exo-cis*-3-methylnorbornane-2-carboxylic acid (14).

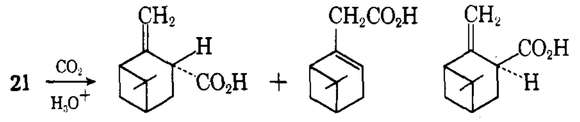


18 19

Metalation of α-Pinene.—The reaction of amylsodium with α-pinene (20) would be predicted to result in the formation of the allylsodium derivative 21, because of preferential exchange at the terminal allylic methyl group.[2,9] Carbonation of 21 could conceivably give rise to three isomeric acids, 22, 23, and 24. When this experiment was carried out, two acids were, in fact, obtained. One of these, crystallized from the crude acid mixture in 18% yield and after purification, had m.p. 98–98.5°. The assignment of structure 22 to this acid stemmed from the occurrence of absorption bands in the infrared due to a nonconjugated carboxyl group (1715 cm.$^{-1}$) and to a terminal methylene group (1640 and 895 cm.$^{-1}$). In addition, the ultraviolet spectrum showed only end absorption. Finally, the n.m.r. spectrum provided conclusive evidence for the structure as well as the stereochemistry shown in 22. In particular, the spectrum verified the presence of two vinyl hydrogens with one absorbing at τ 4.94 and the other at 5.12. Both of these signals appear as fairly



20 21



22 23 24

---

(13) K. Alder and W. Gunzl, *Chem. Ber.*, **93**, 809 (1960).

(14) The spectra of various other isomeric methylnorbornanecarboxylic acids have been published: R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(15) The signal for the C-1 proton in 4 occurs at τ 7.34.

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

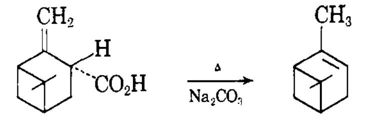
(17) It is possible that acid 8 was in fact formed, but subsequently rearranged to 10 during the isolation. Although strain and resonance factors would contribute to the driving force for rearrangement, the work of others[9] as well as our own observation (*vide infra*) that acid 23 was obtained from α-pinene *exclusive of its conjugated isomer* tends to diminish the likelihood of such a side reaction.

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

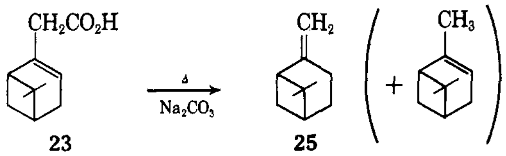
well-resolved triplets with $J = 1.5$ c.p.s. A very broad multiplet with the integral weight of one proton is centered at τ 6.51 and is assigned to the allylic hydrogen on the carboxyl-bearing carbon. The geminal but nonequivalent methyl groups appear as sharp singlets at τ 8.74 and 9.26.[19] The almost identical chemical shifts recorded for the methyl groups in β-pinene (**25**, τ 8.77 and 9.28)[20] demonstrates that the carboxyl group must have the *endo* configuration. If the carboxyl group were in the *exo* position as in **24**, serious interaction with the *syn* methyl group would be expected. Furthermore, this conclusion is in line with the *a priori* expectation that carbonation of the ion **21** from the *exo* side would be very effectively inhibited by the isopropylidene bridge.

Chemical confirmation of structure **22** was obtained by applying the Arnold[11] decarboxylation reaction, which regenerated α-pinene exclusively (eq. 5).

Fractional distillation of the mother liquors from **22** provided a second acid, a liquid with b.p. 115° at 0.5 mm. in 35% yield. This acid was recognized as the known[11] mertenylcarboxylic acid **23** by comparison of its physical properties with literature values and by a study of its infrared and n.m.r. spectrum. Arnold and Danzig[11] had previously effected decarboxylation of **23**, which gives β-pinene (**25**) accompanied by some rearranged olefin. In support of our structural assignment, we have repeated this experiment and obtained the same results (eq. 6).



22 **20** (5)



23 **25** (6)

In conclusion, it should be pointed out that the results with α-pinene constitute the only exception to the generalization (*vide supra*) concerning the composition of the isomeric acids obtained by carbonation of an allylsodium derivative. In this case, the "straight-chain" isomer **23** predominated over the "branched-chain" isomer **22** by a factor of 2 to 1.

Experimental

The infrared spectra were taken on a Perkin-Elmer Infracord (Model 137 B), the ultraviolet spectra on a Perkin-Elmer 202, and the n.m.r. spectra on a Varian Associates A-60 spectrometer. Microanalysis were performed by Dr. A. Bernhardt, Mülheim, Germany. The melting points were taken on a Fisher-Johns melting point block and are uncorrected.

Metalation of Camphene (1).—To 0.154 mole of amylsodium–sodium chloride[21] suspended in pentane was added 17.2 g. (0.126 mole) of *dl*-camphene. The bottle was sealed under helium and was shaken occasionally. After 69 days at room temperature the remainder was carbonated with an excess of solid carbon dioxide. The carbonation product was hydrolyzed and filtered, and the alkaline solution was extracted four times with 200-ml. portions of ether. The aqueous layer was made acidic (concentrated H_2SO_4), extracted twice with 250-ml. portions of ether, saturated with sodium chloride, and extracted five times with 250-ml. portions of ether. The combined ether extracts were dried ($CaSO_4$) and after filtration and evaporation gave 11.34 g. of crude product. This was dissolved in ether, and the solution was evaporated to small volume and refrigerated. Crystallization from the ether solution gave 4.05 g. of 3,3-dimethyl-2-norbornylideneacetic acid (**3**), m.p. 114–121°. Recrystallization from ether raised the melting point to 128–129°. An analytical sample prepared by sublimation (80° at 0.05 mm.) melted at 129.5–130.0° (lit.[7] m.p. 127.5°): $\nu_{\max}^{\mathrm{KBr}}$ 1690 cm.$^{-1}$, $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 227 mμ (log ϵ 4.17).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; neut. equiv., 180. Found: C, 73.50; H, 8.82; neut. equiv., 184.

Distillation of the mother liquor gave 0.156 g. of **3**, m.p. 118–123° (mixture melting point with an analytical sample, 118.0–124.5°), and 0.522 g. of caproic acid, identified by its infrared spectrum. The total yield of **3**, based on unrecovered hydrocarbon, was 33.7%.

Metalation of Norcamphene (4).—To a pentane suspension of 0.154 equiv. of amylsodium–sodium chloride was added 17.28 g. (0.16 mole) of norcamphene (**4**). The container was flushed with helium, sealed, and shaken frequently during the reaction period. After 37 days the reaction mixture was carbonated with an excess of solid carbon dioxide. After the product was hydrolyzed and filtered, the aqueous layer was extracted with three 100-ml. portions of ether. The aqueous layer was made acid (dilute HCl), extracted three times with 100-ml. portions of ether, saturated with sodium chloride, and then extracted five times with 100-ml. portions of ether. The combined ether extracts were dried over calcium sulfate, filtered, and flash evaporated to leave 15.01 g. of yellow oil. A fractionation of the crude product afforded 1.20 g. of caproic acid (identified by the infrared spectrum) and 6.882 g. of clear liquid boiling at 97–98° at 0.25 mm. This sample was redistilled to give 5.846 g. (29%) of material, from which 2.451 g. of *exo*-3-methylenenorbornane-2-carboxylic acid (**6**) was obtained by crystallization (10.4% yield, also based on unrecovered hydrocarbon).[22] Two recrystallizations from petroleum ether (b.p. 65–110°) gave a sample melting at 61.0–61.5°: $\nu_{\max}^{\mathrm{KBr}}$ 1705, 1660, 895, and 875 cm.$^{-1}$. Further recrystallization did not raise the melting point. The ultraviolet spectrum showed only end absorption.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95; neut. equiv., 152. Found: C, 71.45; H, 7.71; neut. equiv., 153.

The mother liquors were distilled (80° at 0.025 mm.) to give 1.794 g. of liquid with an infrared spectrum almost identical with that of **6**. Indeed, **6** slowly crystallized from this distillate. The nonvolatile residue was discarded.

The pot residue from the fractionation of the original crude product was distilled (110° at 0.1 mm.) to give 1.165 g. of crystalline 2-norbornylideneacetic acid (**10**), m.p. 64–69° (5.0% yield, based on unrecovered hydrocarbon), and a nonvolatile residue, which was discarded. This acid (**10**) was recrystallized four times from petroleum ether (b.p. 65–110°) to give a sample melting at 116.5–117.0°: $\nu_{\max}^{\mathrm{KBr}}$ 1680 cm.$^{-1}$, $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 228 mμ (log ϵ 4.05).

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.21; H, 7.78.

Pyrolysis of *exo*-3-Methylenenorbornane-2-carboxylic Acid (6). Formation of 2-Methylnorbornene (13).—A sample of **6** weighing 0.219 g. was mixed with 0.0146 g. of anhydrous sodium carbonate and was heated to 180° to give 2-methylnorbornene (**13**), identified by its n.m.r. spectrum,[12] uncontaminated by **4**.

Hydrogenation of *exo*-3-Methylenenorbornane-2-carboxylic Acid (6). Preparation of *exo-cis*-3-Methylnorbornane-2-carboxylic Acid (14).—A 122-mg. sample of **6** was dissolved in 5 ml. of 95% ethanol with 20 mg. of previously reduced 5% palladium-on-carbon catalyst. Upon treatment with hydrogen (magnetic stirring) for 25 min. 1.09 equiv. of hydrogen were taken up. Filtration and evaporation of the solvent left 0.113 g. of crystal-

---

[19] The n.m.r. spectrum of **22** showed, in addition, the acidic proton at τ −1.7, a doublet (J = 10 c.p.s., weight of one hydrogen) centered at τ 8.46, and a series of reasonably well-resolved lines between τ 7.4 and 8 which account (in integral weight) for the remaining five hydrogens.

[20] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalogue," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 274.

[21] See ref. 53 in paper VII.

[22] Gas chromatographic analysis indicated no significant amount of rearranged olefin accompanying the recovered starting material.

line **14**, m.p. 87–98°. Two recrystallizations from petroleum ether (b.p. 65–110°) gave **14** melting at 112.0–112.5° (lit.[13] m.p. 114–115°).

Metalation of α-Pinene (20).—To 0.183 mole of amylsodium–sodium chloride suspension in pentane was added 25.0 g. (0.183 mole) of α-pinene. The container was sealed under helium and was shaken occasionally during the reaction period. After 59 days the reaction mixture was carbonated with an excess of solid carbon dioxide. The product was hydrolyzed, filtered, and extracted three times with 150-ml. portions of ether. The aqueous layer was acidified (dilute H_2SO_4), extracted twice with 200-ml. portions of ether, saturated with sodium chloride, and extracted five times with 150-ml. portions of ether. The combined ether extracts were dried over calcium sulfate, filtered, and evaporated to yield 28.947 g. of yellow oil. From the crude acid there crystallized 2.392 g. of white, crystalline *endo*-2(10)-pinene-3-carboxylic acid (**22**), m.p. 90–95°, and a second crop (0.190 g.) of **22** melting at 81.5–89.0°. The acid was recrystallized three times from petroleum ether (b.p. 65–110°) to give 1.064 g. of **22** melting at 98.0–98.5° (further recrystallization did not raise the melting point), showing $\nu_{\max}^{\text{KBr}}$ 1640 and 895 cm.$^{-1}$. The ultraviolet spectrum showed only end absorption.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; neut. equiv., 180. Found: C, 73.34; H, 8.71; neut. equiv., 182.

A third crop of **22** (3.056 g.), m.p. 73–83°, crystallized from the mother liquor and was identified as **22** by the infrared spectrum and the undepressed mixture melting point. The yield of **22**, based on unrecovered hydrocarbon, was 18.3%. The mother liquor was distilled to a temperature of 100° at 0.1 mm. to give 17.946 g. of liquid. The liquid was fractionated to give 1.345 g. of caproic acid, identified by the infrared spectrum, and 10.627 g. (34.5% yield, based on unrecovered hydrocarbon) of the known mertenyl carboxylic acid (**23**), b.p. 115° at 0.5 mm. (lit.[11] b.p. 95° at 0.05 mm.), and a nonvolatile residue. The acid **23** was identified by its n.m.r. spectrum and by pyrolysis. A 0.55-g. sample of **23** was mixed with 0.031 g. of anhydrous sodium carbonate and was pyrolyzed at 180° to give a mixture[11] of α- and β-pinenes which were identified by gas chromatography.

Paracyclophanes. III. Octamethyl[2.2]paracyclophane. A Highly Strained Cyclophane[1]

Daniel T. Longone and Lydia H. Simanyi

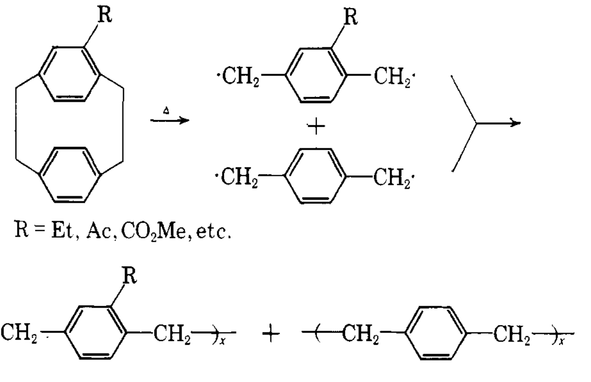
Department of Chemistry, University of Michigan, Ann Arbor, Michigan

Received June 26, 1964

The Hofmann-type pyrolysis of pentamethylbenzyltrimethylammonium hydroxide has been investigated as a route to octamethyl[2.2]paracyclophane (tetramethyl-*p*-xylylene dimer). This dimer, isolated in low yield, represents an extreme case of transannular eclipsing of alkyl groups. Such eclipsing leads to destabilization of the already strained [2.2]paracyclophane system. Other products formed in the pyrolysis reaction, in addition to high-melting polymer, are pentamethylbenzyl alcohol, the corresponding ether, and the tetramethyl-*o*-xylylene dimer, octamethyldibenzocyclooctadiene.

The synthesis and properties of a wide variety of [*m.n*]paracyclophanes have been extensively investigated by Cram's group.[2] Ample evidence has been presented for the existence of transannular electronic and steric effects in the reactions and physical properties of these ring systems. Due to its synthetic accessibility,[3] and its rigid and unique geometry, [2.2]-paracyclophane (**1**) holds a central position in this series. A refined X-ray analysis of the structure, thermal expansion, and molecular vibrations of **1** at 93°K. and at room temperature has been described recently.[4] The maximum separation between benzene rings (*ortho* carbons) is 3.09 Å., while the *para* carbons are only 2.75 Å. apart (Fig. 1). Puckering of the rings is achieved by increasing the bond angles (*θ*) between the methylene bridges and the benzene rings from 90 to 111° and by folding the rings (through 14°) away from each other along the line of the *para* carbon atoms. At room temperature the bond length between the methylene carbon atoms is 1.63 Å., but this reduces to 1.56 Å. at 93°K.

This strained system should exhibit more or less facile thermolysis of the bridge methylene bonds, its susceptibility to such cleavage modified by the electronic and steric effects of appropriate substituents. A systematic study of the stability of [2.2]paracyclophane and its derivatives is lacking; however, fragmentary information is available in the literature. While hydrocarbon **1** appears stable up to its melting point (287°), it has been pyrolyzed to polymer at 550°[5] and affords[6] both 4,4′-dimethylbibenzyl and *p,p*′-dimethyl-*trans*-stilbene on prolonged heating to 400°. Vapor phase pyrolysis (550–600°) of a variety of aryl-substituted derivatives of **1** (ethyl, acetyl, carbomethoxy, dibromo, dichloro, and trichloro) yields[5] the monomeric *p*-xylylenes evidenced by the isolation of the corresponding homopolymers, the latter formed subsequent to a fractional condensation technique.



Increased nuclear substitution, especially by aromatic moieties, can lead to destabilization of the cyclophane ring system. Benzo[2.2]paracyclophane (**2**) and

---

[1] Research supported in part by the U. S. Army Research Office (Durham). For previous papers in this series, see (a) D. T. Longone and F.-P. Boettcher, *J. Am. Chem. Soc.*, **85**, 3436 (1963); (b) D. T. Longone and C. L. Warren, *ibid.*, **84**, 1507 (1962).

[2] D. J. Cram and L. A. Singer, *ibid.*, **85**, 1084 (1963), and previous papers in this series.

[3] H. E. Winberg and F. S. Fawcett, *Org. Syn.*, **42**, 83 (1962). A number of monosubstituted [2.2]paracyclophanes are known: L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963).

[4] K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc.* (London), **A255**, 82 (1960). For an earlier study, see C. J. Brown, *J. Chem. Soc.*, 3265 (1953).

[5] W. F. Gorham, German Patent 1,085,673 (1960); *Chem. Abstr.*, **55**, 22920 (1961).

[6] J. R. Schaefgen, *J. Polymer Sci.*, **15**, 203 (1955).