

hindered olefin, 2,3-dimethyl-2-butene, where hydroboration at 25° was slow, requiring approximately 24 hr, was there identified 1% of 2,3-dimethyl-1-butanol, evidently arising from a small amount of isomerization.

The results are summarized in Table II.

Rates of hydroboration were determined by placing 25 ml of 0.78 *M* 9-BBN<sup>8</sup> in THF in the usual hydroborating flask, followed by 5 ml of a 2.00 *M* solution of olefin in THF. The reaction mixture was maintained at 25° and aliquots were removed at appropriate intervals of time and analyzed by hydrolysis for residual hydride. For preparation of alcohols the hydroboration was carried out in a similar manner. Then 5 ml of 6 *M* sodium hydroxide was added, followed by the addition of 4 ml of 30% hydrogen peroxide. The reaction mixture was heated at 60° for 1 hr to ensure completion of the oxidation (the adduct of 9-BBN with 2,3-dimethyl-2-butene was particularly slow to oxidize). To isolate the product, the reaction mixture was cooled to 25°, the aqueous phase saturated with potassium carbonate, and the dry THF phase analyzed by glpc using an internal standard of *p*-dimethoxybenzene.

It is evident that the commercial availability of 9-BBN will make selective hydroboration an exceedingly simple laboratory operation.

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Received August 2, 1968

### The Reaction of Carbon Monoxide with B-Alkyl-9-borabicyclo[3.3.1]nonanes. A Remarkably Simple Synthesis of 9-Alkylbicyclo[3.3.1]nonan-9-ols

Sir:

The reaction of carbon monoxide with organoboranes<sup>1</sup> produced *via* hydroboration<sup>2</sup> provides convenient synthetic routes to tertiary alcohols,<sup>3a</sup> secondary alcohols,<sup>3b</sup> acyclic<sup>3b,c</sup> and cyclic ketones,<sup>3d</sup> including those with functional groups,<sup>3e,f</sup> methylol derivatives,<sup>3g</sup> aldehydes,<sup>3h</sup> and polycyclic compounds.<sup>3i</sup> We now wish to report that the B-alkyl-9-borabicyclo[3.3.1]nonanes, now readily available *via* the cyclic hydroboration-isomerization of 1,5-cyclooctadiene<sup>4</sup> and the reaction of the 9-BBN intermediate with olefins,<sup>5</sup> undergo carbonylation cleanly and in high yield to produce the corresponding 9-alkylbicyclo[3.3.1]nonan-9-ols (1).

(1) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); **85**, 892, 1636 (1963).

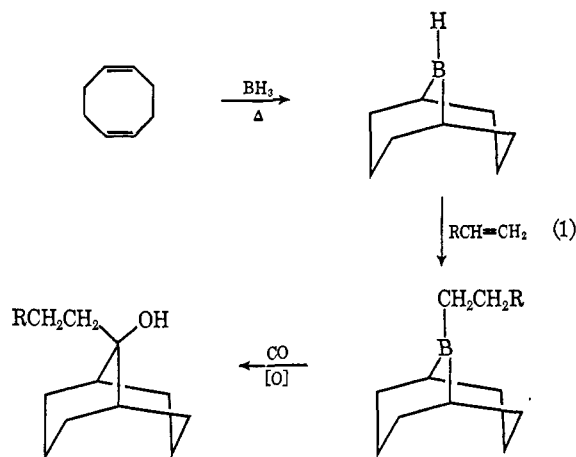
(2) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(3) (a) H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 2737 (1967); (b) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2738 (1967); (c) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 4528 (1967); (d) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967); (e) H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967); (f) H. C. Brown and E. Negishi, *ibid.*, **89**, 5285 (1967); (g) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2740 (1967); (h) H. C. Brown, R. A. Coleman, and M. W. Rathke, *ibid.*, **90**, 499 (1968); (i) H. C. Brown and E. Negishi, *ibid.*, **89**, 5478 (1967).

(4) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280 (1968).

(5) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5281 (1968).

This procedure provides a remarkably simple entry into this new interesting series of carbinols in which both the 9-alkyl and 9-hydroxy groups are bonded axially to a six-membered ring.



With but two exceptions, the yields were in the range of 85–95%. Indeed, it is remarkable that groups such as isobutyl, 2,3-dimethyl-1-butyl, and cyclohexyl can be introduced into the 9 position without apparent difficulty.

The following procedure is representative. 9-BBN was produced by the dropwise addition of 10.8 g (100 mmol) of 1,5-cyclooctadiene to a flask containing 40 ml of 2.5 *M* borane in THF under nitrogen. The solution was heated under reflux for 1 hr and cooled to 25°, and 7.0 g (100 mmol) of 1-pentene added. After 1 hr (to ensure complete hydroboration) the solution was transferred with a syringe to an autoclave flushed with nitrogen; 10 ml of ethylene glycol was then added. The autoclave was pressured to 70 atm with carbon monoxide and the temperature was raised to 150° and maintained there for 24 hr. The contents were oxidized with 50 ml of 6 *M* sodium hydroxide and 40 ml of 30% hydrogen peroxide at 50–60°. The reaction mixture was maintained at this temperature for 2 hr to complete the oxidation. The flask was cooled, the aqueous phase was saturated with potassium carbonate, and the crude product was isolated by removal of the THF on a rotary evaporator. There was obtained 18.0 g (86%) of 9-*n*-pentylbicyclo[3.3.1]nonan-9-ol, 95% pure by glpc. Redistillation, bp 106° (0.15 mm), gave the pure alcohol, *n*<sup>20</sup><sub>D</sub> 1.4967. The results are summarized in Table I.

The assigned structure was confirmed by degradation of the 9-*n*-pentylbicyclo[3.3.1]nonan-9-ol to the known bicyclo[3.3.1]nonan-9-one.<sup>6</sup> Treatment of 9-*n*-pentylbicyclo[3.3.1]nonan-9-ol with phosphorus oxychloride in pyridine<sup>7</sup> afforded a single olefin in 92% yield (bp 88–92° (1.5 mm), *n*<sup>20</sup><sub>D</sub> 1.4903). The olefin showed only one vinyl proton (a triplet at 5.15 ppm), consistent with 9-*n*-pentylidenebicyclo[3.3.1]nonane. This olefin was then treated with ozone (–78° in chloroform) and then oxidized in hydrogen peroxide–acetic acid to give 30% bicyclo[3.3.1]nonan-9-one, mp 154–156°, 2,4-dinitro-

(6) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

(7) R. R. Sauers, *J. Am. Chem. Soc.*, **81**, 4873 (1959).

**Table I.** Physical Properties of 9-Alkylbicyclo[3.3.1]nonan-9-ols Produced *via* Carbonylation of B-alkyl-9-borabicyclo[3.3.1]nonanes

9-Alkyl	Mp or bp (mm), °C	$n_D^{20}$	Anal, %				Yield, <sup>a</sup> %	<i>p</i> -Nitrobenzoate mp, °C (pentane)
			C, calcd	H, calcd	C, found	H, found		
Ethyl	62.8–63.2		78.51	11.78	78.80	11.99	90.3	126.5–127.5
1-Pentyl	106 (0.15)	1.4967	79.93	12.46	79.79	12.70	85.5	93.5–94.0
Isobutyl	94 (1.0)	1.4982	79.53	12.32	79.37	12.47	86.5	103.8–104.0
3-Methyl-2-butyl	95 (0.5)	1.5011	79.93	12.46	80.23	12.59	31.0 <sup>b</sup>	137 dec
2,3-Dimethyl-1-butyl	105 (0.3)	1.4988	80.29	12.58	80.23	12.70	85.0	130 dec
Cyclohexyl	108.0–108.2		81.02	11.79	81.23	11.84	96.8	180 dec
Cyclopentyl	77.7–78.1		80.71	11.61	80.62	11.67	46.4 <sup>c</sup>	180 dec

<sup>a</sup> Yields are of isolated crude alcohol of about 95% purity. <sup>b</sup> Two other products were formed in about equal yields: *cis*-5-hydroxycyclooctyl 3-methyl-2-butyl ketone and a second tertiary alcohol, presumably the 3-methyl-1-butyl isomer formed by a rearrangement of the organoborane. <sup>c</sup> A second product formed in about equal yield was (*cis*-5-hydroxycyclooctyl)cyclopentylcarbinol.

phenylhydrazone mp 190.0–190.2° (lit.<sup>6</sup> mp 155–158.5°, 2,4-DNP mp 191.8–192.3°).

We attempted to achieve the synthesis of bicyclo[3.3.1]nonan-9-one directly by carrying out the carbonylation of appropriate B-alkyl derivatives in the presence of water.<sup>3b</sup> However, the products indicated that the B-alkyl group migrates in preference to the bridging boron-carbon bonds. Thus, after carbonylating at 100°, the B-*n*-pentyl derivative yielded 32% *cis*-1,5-cyclooctanediol (from uncarbonylated organoborane), 34% 9-*n*-pentylbicyclo[3.3.1]nonan-9-ol, and 34% of a third component identified as *cis*-5-hydroxycyclooctyl *n*-pentyl ketone. The isobutyl derivative gave similar results. The *thexyl*<sup>3d,f</sup> derivative failed to carbonylate prior to rearrangement of the *thexyl* group to the 2,3-dimethyl-1-butyl grouping.<sup>8</sup> Consequently, the best available route to the 9-ketone proceeds through the tertiary alcohol, as utilized in the degradation sequence.

In many of the new reactions utilizing organoboranes for synthetic purposes,<sup>3h,9</sup> only one of the three groups on boron are utilized. The observation that the B-alkyl group in B-alkyl-9-BBN undergoes preferential migration during the carbonylation reaction suggests the possibility of utilizing these derivatives to overcome this difficulty.<sup>10</sup>

We previously demonstrated that hydroboration-carbonylation-oxidation serves as a new, convenient route to monocyclic<sup>3d</sup> and unbridged polycyclic<sup>3i,11</sup> structures. The present study establishes that this procedure also provides a remarkably simple route to a bridged polycyclic, the bicyclo[3.3.1]nonane structure. We are presently examining the cyclic hydroboration of cycloheptadiene, cyclohexadiene, and cyclopentadiene followed by carbonylation of the intermediates in

(8) The B-*thexyl*-9-borabicyclo[3.3.1]nonane molecule is evidently severely sterically hindered. Its oxidation by alkaline hydrogen peroxide is unusually difficult.

(9) J. J. Tufarillo, L. T. C. Lee, and P. Wojkowski, *J. Am. Chem. Soc.*, **89**, 6804 (1967); A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. E. Rathke, *ibid.*, **89**, 5708 (1967); H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968).

(10) Indeed, we have achieved considerable success in this endeavor (research in progress with E. F. Knights, M. W. Rathke, and M. M. Rogić). We hope to report these results shortly.

(11) H. C. Brown and E. Negishi, *Chem. Commun.*, 594 (1968).

an attempt to establish the scope and possible limitations of this new synthesis of bridged polycyclics.<sup>12</sup>

(12) Research in progress with P. Burke.

(13) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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#### Flash Vacuum Pyrolysis. IV. The Isolation and Rearrangement of 9,10-Dihydrofulvalene<sup>1</sup>

Sir:

Although substantial physical<sup>2</sup> and theoretical<sup>3</sup> data have been obtained on the cyclopentadienyl radical, very little is known about its simplest chemistry. Our initial investigation of this species<sup>1a</sup> was based on its formation by flash vacuum pyrolysis (fvp) of allyl phenyl ether, most likely through the intermediacy of the phenoxy radical which decarbonylates.<sup>2a</sup> We found that allylcyclopentadiene and biallyl were the predominant stable products resulting from the rapid quenching of the pyrolysate on a liquid nitrogen cooled surface. The product formed from coupling of two cyclopentadienyl radicals was not detected even though our mass spectral investigation<sup>4</sup> of the pyrolysis indicated the presence of the dimer in the gas phase.

Recently we have found that the same dimer is generated, along with cyclopentadienyl and nickelcyclopentadienyl radicals, when nickelocene is pyrolyzed in an oven coupled directly to the ionization chamber of

(1) (a) Part I: E. Hedaya and D. W. McNeil, *J. Am. Chem. Soc.*, **89**, 4213 (1967); (b) part II: C. L. Angell, E. Hedaya, and D. McLeod, *ibid.*, **89**, 4214 (1967); (c) part III: Paul Schissel, D. J. McAdoo, and E. Hedaya, to be published.

(2) (a) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960); (b) R. F. Pottie and F. P. Lossing, *ibid.*, **85**, 269 (1963); (c) S. Ohnishi and S. Nitta, *J. Chem. Phys.*, **39**, 2848 (1963); (d) P. Zandstra, *ibid.*, **40**, 612 (1964); (e) R. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964); (f) G. R. Liebling and H. M. McConnell, *J. Chem. Phys.*, **42**, 3931 (1965); (g) G. Porter and B. Ward, *Proc. Roy. Soc.*, **A303**, 139 (1968); G. Porter and B. Ward, *Proc. Chem. Soc.*, 288 (1964).

(3) (a) N. Bouman, *J. Chem. Phys.*, **35**, 1661 (1961); (b) H. C. Longuet-Higgins and K. L. McEwen, *ibid.*, **26**, 719 (1957); (c) F. A. Cotton and G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 5764 (1952); (d) A. Streitwieser, Jr., *ibid.*, **82**, 4123 (1960); (e) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

(4) P. Schissel, D. J. McAdoo, and E. Hedaya, unpublished results.