which contains magnetically nonequivalent silylene protons (the structure of C_2 symmetry is logically to be expected from rearrangement of the bridged isomer A). At 150°, II undergoes further reaction yielding *closo*-$C_3B_3H_7$,[9] 4-$SiH_3C_2B_4H_7$, $C_2B_4H_8$, and solids.

Attempts to prepare the dimethylsilylene analog of I, μ,μ'-$Si(CH_3)_2(C_2B_4H_7)_2$, by reaction of $Si(CH_3)_2Cl_2$ with $NaC_2B_4H_7$ have been unsuccessful, suggesting possible inhibition by close steric interaction of the methyl groups with the carborane cages.

Acknowledgments. We are grateful to Mr. Richard Torian and Dr. Vernon Miller for assistance in obtaining the mass spectra and nmr spectra, respectively. This work was supported by the Office of Naval Research.

(9) M. L. Thompson and R. N. Grimes, *J. Amer. Chem. Soc.*, **93** 6677 (1971).

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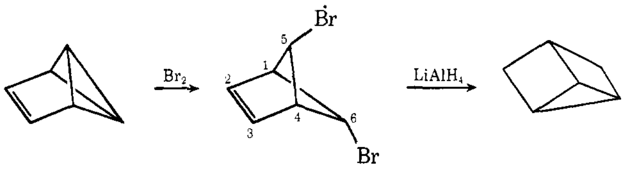
Uses of Benzvalene in Synthesis. A Synthesis of Tricyclo[2.2.0.0^{2,6}]hexane

Sir:

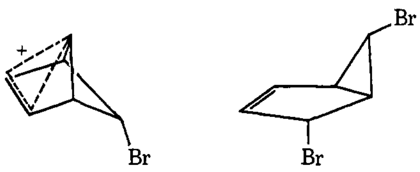
Since the valence tautomer of benzene, benzvalene (I), has become readily available,[1] we have been studying its chemistry, and we are reporting here its uses in the synthesis of other ring systems. Particularly interesting is a conversion of benzvalene in two steps, as shown in Scheme I, to tricyclo[2.2.0.0^{2,6}]hexane (III),[2] the parent of a ring system that is very simple, yet extremely rare.[2,3]

Scheme I



I II III

If one considers the large number of interesting products that might result after electrophilic attack on benzvalene, the observed result of bromine addition, that only a single product forms, seems remarkable,[4] especially as the isomer formed is not the thermodynamically favored one and the double bond, a usual site of electrophilic attack, is unaffected.[5] The solitary product has structure II. It is formed when 5% bromine in CCl_4 is added to solutions of benzvalene in ether at −10 to 0° until the bromine color no longer discharges.[7] The yield, determined using proton nmr spectroscopy after solvents are removed at 0° and reduced pressure, is quantitative.[8] The structure of the product is proven by its reduction[9] giving bicyclo[2.1.1]hexane,[11] and by its proton nmr spectrum showing expectedly simple resonances[12] including two of characteristic multiplicity[13] for the protons adjacent to bromine atoms. The reason bromine adds to benzvalene as it does is possibly that initial electrophilic attack occurs from behind the central bond, where electron density is concentrated,[14,14e] to give carbonium ion IV, which like analogous species is stabilized by delocalization and reacts stereospecifically with nucleophiles.[15]



IV V

The dibromide II is thermally unstable, carbon tetrachloride solutions rearranging to *exo,anti*-4,6-dibromobicyclo[3.1.0]hexene (V)[16] in 98% yield with a half-life of 2 hr at 37°.[17,17a] The structure of the rearrangement product is proven by its reduction[18] giving bicyclo[3.1.0]hexene[20] and by its proton nmr spectrum showing

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[1] T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971). Yields now average 45%.

[2] D. M. Lemal and K. S. Shim, *ibid.*, **86**, 1550 (1964).

[3] (a) J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966); (b) S. Masamune and K. Fukumoto, *Tetrahedron Lett.*, 4647 (1965).

[4] The dihydro derivative, tricyclo[3.1.0.0^{4,6}]hexane [D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 3231 (1964)], with Br_2 in CCl_4 gives complex material.

[5] Aqueous acid gives bicyclo[3.1.0]hexen-4-ol.[1,6]

[6] J. A. Berson and N. M. Hasty, Jr., *J. Amer. Chem. Soc.*, **93**, 1549 (1971).

[7] The halogens must inductively protect the olefin [*cf.* J. R. Shelton and L. Lee, *J. Org. Chem.*, **25**, 428 (1960)].

[8] The measured yield was 100.3% with nitrobenzene as internal standard.

[9] Hydrogenation (PtO_2, ethyl acetate); then $(C_6H_5)_3SnH$ to remove bromine.[10]

[10] H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963).

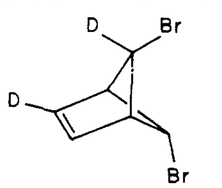
[11] The nmr spectrum is distinctive: R. Srinivasan, *J. Amer. Chem. Soc.*, **83**, 4923 (1961).

[12] In CCl_4: τ 3.22 (H_2, J = 2.0 Hz, triplet), 6.85 (H_1, $J \approx$ 2.0 Hz, quartet), 4.14 (H_6, J = 2.0 Hz, triplet), 5.37 (H_5, singlet).

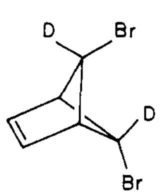
[13] J. R. Scheffer and R. A. Wostradowski, *Chem. Commun.*, 144 (1971), and references therein.

[14] (a) M. Pomerantz and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **88**, 3970 (1966); (b) M. Pomerantz, G. W. Gruber, and R. M. Wilke, *ibid.*, **90**, 5040 (1968); (c) J. M. Schulman and G. J. Fisanick, *ibid.*, **92**, 6653 (1970); (d) M. D. Newton and J. M. Schulman, *ibid.*, **94**, 767 (1972).

[14e] NOTE ADDED IN PROOF. Deuterium labeling experiments show that this is only in part correct. The major pathway from I to II is initiated by attack on the double bond followed by a Wagner–Meerwein rearrangement. Benzvalene deuterated at C_5 and C_6 (n-BuLi–ether, D_2O, twice, 94% deuterated) gives i and ii in the ratio 87:13 [integration of the proton nmr: τ 3.22 ($H_{2,3}$, m, 1.24 H), 4.14 (H_6, t, 0.92 H), 5.37 (H_5, s, 0.065 H), 6.85 ($H_{1,4}$, t, 1.90 H)].



i



ii

[15] (a) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *ibid.*, **91**, 4322 (1969); (b) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

[16] Analyses for C, H, and Br were satisfactory.

[17] At least three mechanisms can be imagined. One has been suggested for analogs [ref 15a and W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969)].

[17a] NOTE ADDED IN PROOF. Deuterium labeling experiments show that this mechanism, in which the C_5 bridge migrates with inversion of configuration, is correct here.

[18] $LiAlH_4$ (72% yield) and then[19] Na, *tert*-butyl alcohol, and THF (68% yield).

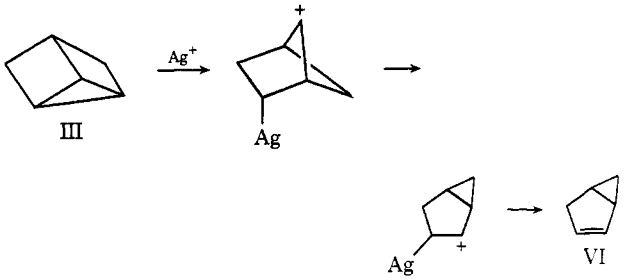
[19] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

[20] (a) J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, **88**, 2850 (1966); (b) G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964).

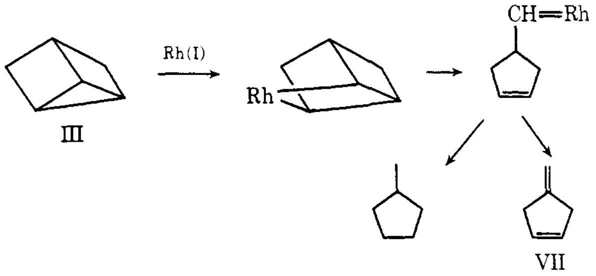
the expected resonances.[21] Despite its thermal instability, II can be reduced at 0° in ether with excess $LiAlH_4$ to give after aqueous work-up and distillation a 76% yield of C_6H_8 hydrocarbons, consisting[26] mainly (82%) of tricyclohexane III,[2] as indicated in Scheme I, contaminated with 18% of bicyclo[3.1.0]hexene.[20] Presumably the reaction giving III is analogous to the reduction of 7-chloronorbornadiene, which gives tricyclo[2.2.1.0^{2,7}]hept-5-ene,[27] but we have been unable to isolate 3-bromotricyclo[2.2.0.0^{2,6}]hexane.[28]

This simple synthesis provides tricyclohexane III in much larger quantities than were previously available.[2] Extending the discovery of Lemal and Shim that hydrogenation of III with palladium catalyst gives mainly methylcyclopentane and some bicyclo[2.1.1]hexane,[2] and extending discoveries in our laboratory that strained hydrocarbons are dimerized and isomerized by hydrogenation catalysts and related substances in the absence of hydrogen,[29] we studied the effects on III of $[Rh(CO)_2Cl]_2$ and AgX (X = PF_6 or BF_4), catalysts now recognized as particularly effective[29f,g,30-32] and different.[33] Both transform III into bicyclo[3.1.0]hexene (VI)[20] and 4-methylenecyclopentene (VII),[36] but the rhodium catalyst gives mainly the latter[37] and the silver mainly the former.[38] This is in accord with analogies for the mechanisms depicted in Schemes II[39] and III.[29d,e,h,31] The latter also provides a particularly simple explanation for results that have previously been explained only with difficulty, why palladium-catalyzed hydrogenolysis of III gives methylcyclopentane, and of a bicyclo[1.1.0]butane with deuterium gives a 3-methylalkene doubly labeled on the methyl.[40]

Scheme II



Scheme III



Acknowledgments. We are grateful to the National Science Foundation (NSF-GP-30669X) for its support.

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(21) In CCl_4: τ 3.91, 4.26 ($H_{2,3}$, J = 5.6 Hz, doublets), 5.11 (H_4, multiplet, $W_{1/2}$ = 4.5 Hz),[22] 7.33 ($H_{1,5}$, multiplet), 7.77 (H_6, J = 2.0 Hz, triplet).[25]

(22) $|J_{4,5}|$ should be 6 Hz if the protons are cis[23] and 2 Hz if trans.[23c,24]

(23) (a) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968); (b) E. Ciganek, *ibid.*, **88**, 2882 (1966); (c) E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969).

(24) (a) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *ibid.*, **30**, 771 (1965); (b) P. K. Freeman, F. A. Raymond, and M. F. Grostic *ibid.*, **32**, 24 (1967).

(25) Assigned as endo because of the small splitting [*cf.* W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967); A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965)].

(26) Isolated by glpc (5 ft × 1/4 in. 10% saturated $AgNO_3$ in benzyl cyanide on 45–60 Chromosorb W regular at 35°), and identified by pmr and ir.

(27) P. R. Story, *J. Amer. Chem. Soc.*, **83**, 3347 (1961). Similarly for 7-chloro- or tosyloxynorbornene: S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963); H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

(28) If much less than a fivefold excess of $LiAlH_4$ is used, 2-bromobicyclo[2.1.1]hexane, the HBr adduct of III, is isolated.

(29) (a) J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966); (b) T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, **32**, 1301 (1967); (c) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967); (d) T. J. Katz, N. Acton, and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 206 (1969); (e) T. J. Katz and S. Cerefice, *ibid.*, **91**, 2405 (1969); (f) T. J. Katz and S. Cerefice, *Tetrahedron Lett.*, 2509 (1969); (g) T. J. Katz and S. A. Cerefice, *ibid.*, 2561 (1969); (h) T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6519 (1969); (i) T. J. Katz and S. A. Cerefice, *ibid.*, **93**, 1049 (1971).

(30) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *ibid.*, **91**, 218 (1969).

(31) Rhodium: (a) P. G. Gassman and F. J. Williams, *J. Chem. Soc., Chem. Commun.*, 80 (1972); (b) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971), and earlier work referred to therein.

(32) Silver: (a) L. Friedman, *ibid.*, **89**, 3071 (1967); (b) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *ibid.*, **93**, 1446 (1971); (c) W. Merk and R. Pettit, *ibid.*, **89**, 4787, 4788 (1967); (d) J. Wristers, L. Brener, and R. Pettit, *ibid.*, **92**, 7499 (1970); (e) L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971); (f) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masmune, *J. Amer. Chem. Soc.*, **93**, 1043 (1971).

(33) The products of some silver-catalyzed reactions are substrates for rhodium (ref 29f *vs.* ref 34; ref 35). For different catalysts giving different products see W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **93**, 7345 (1971), and ref 31b.

(34) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

(35) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 6366 (1970).

(36) W. D. Huntsman, J. A. DeBoer, and M. H. Woosley, *ibid.*, **88**, 5846 (1966).

(37) III (0.53 mmol) + $[Rh(CO)_2Cl]_2$ (0.056 mmol) in CCl_4, 10 min at ambient temperature, gave VII and VI (4:1) in 48% yield, plus a dimer (38%) whose structure is still being determined. $[(C_6H_5)_3P]_3RhCl$ in CCl_4, 18 hr at 50°, gave the same products.

(38) III (0.75 mmol) + $AgPF_6$ (0.22 mmol) in CH_2Cl_2, 20 hr at ambient temperature, gave VI and VII (2:1). $AgBF_4$ in $CDCl_3$ gave similar results.

(39) (a) J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971); (b) M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4610 (1971); (c) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

(40) E. Galantay, N. Paolella, S. Barcza, R. V. Coombs, and H. P. Weber, *ibid.*, **92**, 5771 (1970).

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Received March 8, 1972

Intramolecular Photoaddition of Ketenes to Cyclohexenones

Sir:

Considerable attention has been paid in the last few years to the addition of ketenes to double bonds[1] and to the photoaddition of double and triple bonds to α,β-unsaturated ketones.[2] In general, ketenes are not suffi-

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(1) (a) Thap Do Minh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1766 (1970); (b) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970); (c) J. E. Baldwin and J. A. Kopecki, *J. Amer. Chem. Soc.*, **92**, 4874 (1970); (d) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970); (e) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971); (f) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinhein/Bergstr., 1970; (g) H. U. Wagner and R. Gompper, *Tetrahedron Lett.*, 2819 (1970).

(2) (a) P. DeMayo, *Accounts Chem. Res.*, **4**, 41 (1971); (b) P. G. Bauslaugh, *Synthesis*, 287 (1970).