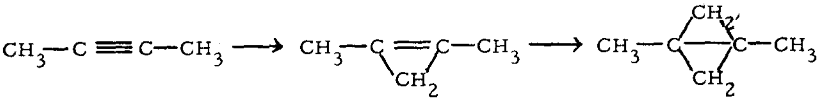
Tetrahedron Letters No.15, pp. 991-995, 1965. Pergamon Press Ltd.
Printed in Great Britain.

1, 3-DIMETHYLBICYCLO[1. 1. 0]BUTANE[1]

W. von E. Doering and J. F. Coburn, Jr.
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut

(Received 11 February 1965)

BICYCLO[1. 1. 0]BUTANE and several derivatives have been synthesized by a variety of methods,[2-9] to which we would like to add the preparation of 1, 3-dimethylbicyclo[1. 1. 0]butane by the addition of methylene to 1, 2-dimethylcyclopropene, itself available by the addition of methylene to butyne-2.[10]

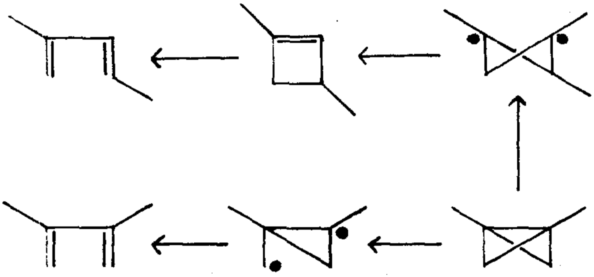


Although neither the photolytic nor the copper-catalyzed reaction of diazomethane with 1, 2-dimethylcyclopropene leads to any bicyclobutane (surprisingly, 1, 2, 3-trimethylcyclopropene is the major product of the former reaction and polymeric material the only product of the latter), modification of the copper-catalyzed reaction by the addition of tri-*n*-butyltin chloride allows the generation of 1, 3-dimethylbicyclo[1. 1. 0]-butane (13%) and 2, 3-dimethylbuta-1, 3-diene (3%) based on unrecovered 1, 2-dimethylcyclopropene. In a more convenient adaptation, butyne-2 may serve as starting material. Purified by distillation or g. l. p. c. on a 2-m silicone column, 1, 3-dimethylbicyclo[1. 1. 0]butane, b.p. 54. 3°, showed N. M. R. peaks at $\delta = 1.34$ (singlet, area 6), 0. 97 (singlet, area 2) and 0. 49 (singlet, area 2) p. p. m. (reported[8] for bicyclobutane, a singlet at 0. 45 p. p. m.).

A remarkably facile addition of iodine, which has been confirmed for bicyclobutane itself,[8] leads to cis-1, 3-diiodo-1, 3-dimethylcyclobutane, m.p. 74.8 - 75.2° (Found: C, 21.2%; H, 2.8%; I, 75.6%. $C_6H_{10}I_2$ requires C, 21.4; H, 3.0; I, 75.6%); δ = 2.11 (singlet, area 6), 2.73 (doublet, area 2) and 3.56 (doublet, J = 15 c.p.s., area 2) p.p.m. The addition is reversed by treatment with lithium aluminum hydride in a reaction which constitutes a second synthesis of 1, 3-dimethylbicyclo[1.1.0]-butane. The reaction appears to be closely related to the recently reported conversion of a 1, 3-diiodoneopentane to a cyclopropane.[11]

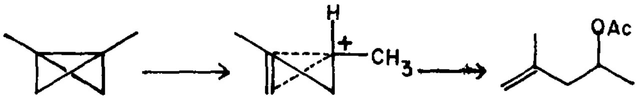
Catalytic hydrogenation in the gas-phase over nickel affords 2-methylpentane whereas hydrogenation in diethylcarbitol over platinum produces a mixture of 2-methylpentane (63%) and cis (32%) - and trans (5%) - 1, 3-dimethylcyclobutane. The two latter products are identical with the products [cis (84%) and trans (16%)] of hydrogenation over platinum of 1-methyl-3-methylenecyclobutane, furnished through the consecutive kindnesses of Professors J. D. Roberts and R. B. Turner [trans isomer: δ = 1.1 (doublet, J = 7 c.p.s., area 6), 1.7 (triplet, J = 7 c.p.s., area 4) and 2.3 (multiplet, area 2) p.p.m.].

Pyrolysis for 1 hr at 255° affords 2, 3-dimethylbuta-1, 3-diene,[12] identified by I. R. and its product of addition with maleic anhydride. This



structural outcome seems to be incompatible with the hypothesis of a prior rearrangement of the cyclopropane-propylene type to 1, 3-dimethylcyclobutene which would be expected to cleave to 2-methylpenta-1, 3-diene instead of the actually observed product.

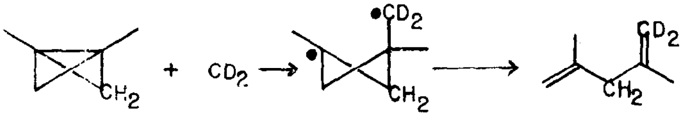
Extraordinarily sensitive to acid, 1, 3-dimethylbicyclo[1. 1. 0]-butane reacts with acetic acid at 25° to give two acetates of which the major one (87. 4%) has been identified by direct comparison with a synthetic sample of 2-acetoxy-4-methyl-pent-4-ene.[13, 14] The major product is one of three expected to result if attack of the proton occurs



at position 1 to give the "bicyclobutonium" ion as intermediate.[15] In these terms,[16] the second methyl group would lead to increased contribution by the allylcarbinyl structure and to increased production of the acyclic acetate.

1, 3-Dimethylbicyclo[1. 1. 0]butane reacts with methylene, generated photolytically from diazomethane, to give 2, 4-dimethylpenta-1, 4-diene *inter alia.* Although the major product, 1-ethyl-3-methylbicyclo-[1. 1. 0]butane (50%) and the minor product, 1, 2, 3-trimethylbicyclo[1. 1. 0]-butane (22%), result from unexceptional insertion into the carbon-hydrogen bond,[17] the unconjugated diene (28%) represents the result of a pathway without parallel in the chemistry of photolytically generated carbenes.

Although the formation of the diene can be conceived to pass through 1, 3-dimethylbicyclo[1. 1. 1]pentane, the completed product of insertion into the 1, 3 carbon-carbon bond (an otherwise unobserved reaction[17] which fails even in the inviting instance of spiropentane[18]), if it be further assumed that this molecule *in statu nascendi* is "hot" enough to undergo thermal reorganization of the cyclobutane type to 2, 4-dimethylpenta-1, 4-diene;[19] this mechanism has been excluded through the employment of dideuteriodiazomethane. The resultant 2, 4-dimethylpenta-2, 4-diene contains no detectable deuterium in the bis-allylic methylene group (δ = 2.68 p.p.m.), but 1.8 atoms of deuterium in the olefinic methylene groups (δ = 4.77 p.p.m.), calculated on the assumption that no deuterium is incorporated into the methyl groups (δ = 1.67 p.p.m.). It is unequivocally concluded that the methylene group originating in the diazomethane becomes one of the olefinic methylene groups in the product.



The absence of deuterium in the bis-allylic methylene group is incompatible with any intermediate having the three-fold symmetry of 1, 3-dimethylbicyclo[1. 1. 1]pentane. It is simplest to hypothesize unsymmetrical attack by methylene, whether singlet or triplet, on the 1, 3 carbon-carbon bond to give an intermediate biradical which, whether paired or unpaired, suffers cleavage, the common fate of 1, 4 biradicals.

REFERENCES AND FOOTNOTES

(1) Taken from the dissertation of J. F. Coburn, Jr., presented February 1963 to Yale University in partial fulfillment of the requirements for the Ph.D. degree. We are deeply indebted to the National Science Foundation (Grant 11378) for its support of this work.

(2) K. B. Wiberg and R. P. Ciula, J. Amer. Chem. Soc. **81**, 5261 (1959).

(3) W. R. Moore, H. R. Ward and R. F. Merritt, J. Amer. Chem. Soc. **83**, 2019 (1961).

(4) W. Mahler, J. Amer. Chem. Soc. **84**, 4600 (1962).

(5) J. Meinwald, C. Swithenbank and A. Lewis, J. Amer. Chem. Soc. **85**, 1880 (1963).

(6) D. M. Lemal, F. Menger and G. W. Clark, *J. Amer. Chem. Soc.* **85**, 2529 (1963).

(7) R. Srinivasan, *J. Amer. Chem. Soc.* **85**, 4045 (1963).

(8) K. B. Wiberg and G. M. Lampman, *Tetrahedron Letters* 2173 (1963).

(9) W. von E. Doering and M. Pomerantz, *Tetrahedron Letters* 961 (1964).

(10) W. von E. Doering and T. Mole, *Tetrahedron* **10**, 65 (1960).

(11) M. S. Newman, J. R. LeBlanc, H. A. Karnes and G. Axelrad, *J. Amer. Chem. Soc.* **86**, 868 (1964).

(12) Discussion of the estimation of the amount of strain in the molecule is given by R. B. Turner, P. Goebel, W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Letters* following communication.

(13) S. A. Ballard, R. T. Holm and P. H. Williams, J. Amer. Chem. *Soc.* **72**, 5734 (1950).

(14) J. Colonge and M. Reymermier, *Bull. Soc. Chim. France* 188 (1956).

(15) For references, see R. Breslow in P. de Mayo, *Molecular Rearrangements* pp. 259-268. Interscience Publishers, New York (1963).

(16) M. S. Silver, M. C. Caserio, H. E. Rice and J. D. Roberts, *J. Amer. Chem. Soc.* **83**, 3671 (1961).

(17) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Amer. Chem. Soc.* **78**, 3224 (1956).

(18) M. Jones, Jr., Ph.D. Dissertation, Yale University, 1963.

(19) Although bicyclo[1.1.1]pentane is now known [K. B. Wiberg, D. S. Connor and G. M. Lampman, *Tetrahedron Letters* 531 (1964)], its behavior on pyrolysis is not reported.