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ADDITIONS OF CARBENES TO 1,2,2-TRIMETHYLBICYCLO[1.1.0]BUTANE[1,2]

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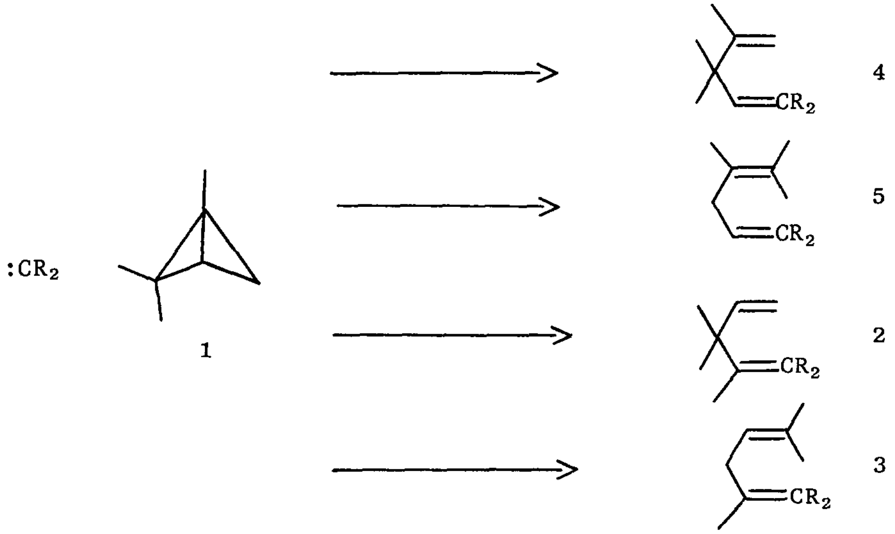
SUMMARY: Dicarbomethoxy- and dichlorocarbene add to 1,2,2-trimethylbicyclo[1.1.0]butane to give derivatives of 2,3,3-trimethylpenta-1,4-diene. These products are not predicted by the mechanism proposed earlier. A new mechanism is suggested.

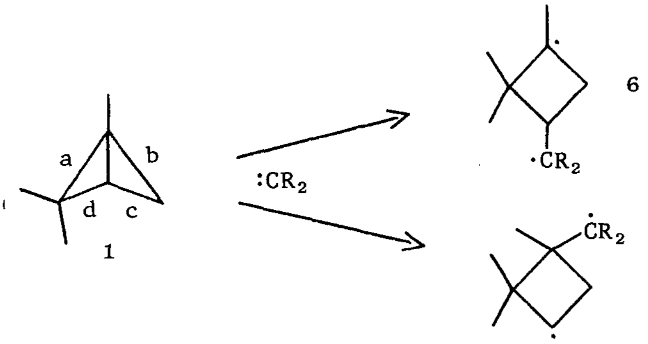
In 1965 Doering and Coburn[3] and Wiberg and his co-workers[4] discovered the formation of 1,4-pentadienes on addition of methylene to bicyclo[1.1.0]butene[4] and its 1,3 dimethyl derivative.[3] More recently Applequist and Wheeler[5] showed that dichlorocarbene gave bicyclo[1.1.1]-pentanes as well as 1,4-pentadienes from substituted bicyclo[1.1.0]butanes. We have remarked[6] that the mechanism proposed[3,4] for this singular reaction seemed unlikely, as it postulated a stepwise addition of two *singlet* carbenes to the central bond of bicyclobutane followed by side bond cleavage. Stepwise additions are rare, if not quite unknown,[7] and there is no

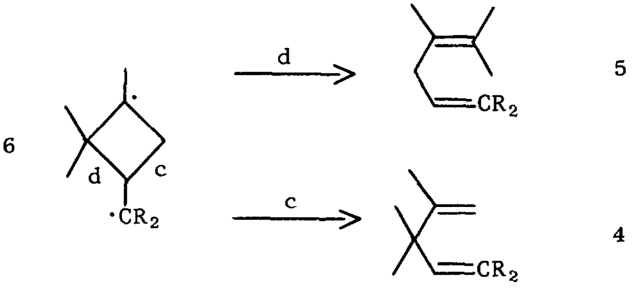


The four possible penta-1,4-dienes from 1.

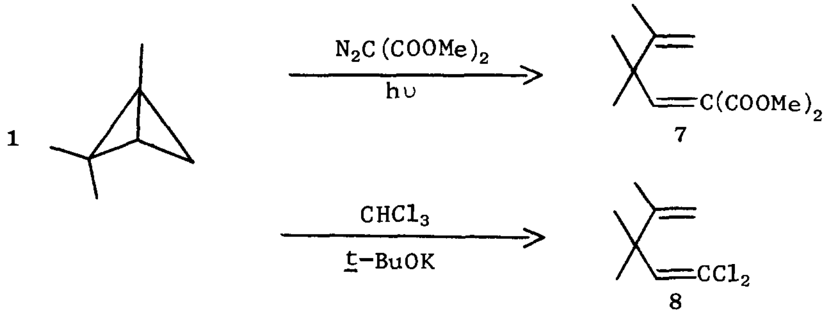
reason to suppose that triplet carbenes could be involved. Here we present experimental evidence that the addition-cleavage mechanism may be incorrect and suggest an alternate.

1,2,2-Trimethylbicyclo[1.1.0]butane (1) was produced from 1,1-dibromo-2,2,3,3-tetramethylcyclopropane by the action of methyllithium and careful, acid-free work-up.[8] In principle, introduction of the three methyl groups allows formation of many products of carbon-hydrogen insertion in addition to the four possible 1,4-pentadienes (2-5). We felt that use of a selective carbene would prejudice the reaction in favor of diene formation and thus excessive complications might be avoided. In addition, use of 1 allows a firm prediction to be made as to the course of the traditional mechanism. Addition of 1 seemed to us certain to occur from the less encumbered "c,d" side to yield the more stable, tertiary radical 6. Intermediate 6 can sever either bond "c" or "d" to give a 1,4-pentadiene. Bond "d" is clearly favored, as breakage leads to 5 in which a tetrasubstituted double bond exists, whereas cleavage of "c" gives 4, containing only a disubstituted double bond.



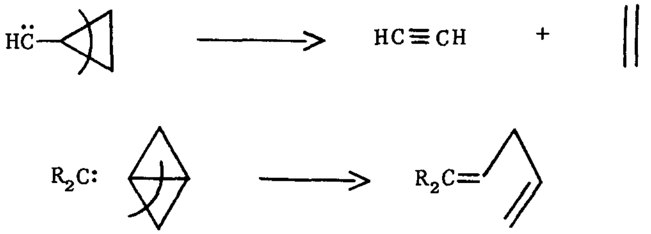


In the event, both direct irradiation of dimethyl diazomalonate and base-induced generation of dichlorocarbene from chloroform led to derivatives of 4. Irradiation of a solution of dimethyl diazomalonate in 1 through Pyrex with a 450-watt Hanovia medium-pressure mercury arc led to four major products. Diester 7 constituted *ca.* 70% of the mixture and was formed in 14% yield. Of the three other products, each consisting of about 10%, only two could be



identified, and these but tentatively, as 1,2,2-trimethyl-3,3-dicarbomethoxybicyclo[1.1.1]-pentane and the bicyclopropyl resulting from addition of the carbene to the vinylcyclopropane formed by acid-catalyzed rearrangement of 1. Compound 7 appears to be the sole 1,4-pentadiene formed. The composition of 7 follows from elemental analysis and a mass spectrometric determination of the precise mass of the parent ion. The detailed structure, and in particular the elimination of structures 2, 3 and 5, follows from an examination of the ^{1}H and ^{13}C NMR spectra. The observation that 7 contains two, terminal methylene protons (δ = 4.85 ppm) serves at a single stroke to rule out the alternate structures. The signals for six equivalent protons at δ = 1.28 ppm and three others at δ = 1.73 ppm show that 7 contains two equivalent methyl groups attached to sp^3 carbon and one attached to a double bond. Finally, the appearance of a single olefinic proton signal at the exceptionally low position of δ = 6.93 ppm is consistent with an "acrylate-like" position β to two ester groups. For comparison, the protons of methyl acrylate appear at δ = 6.35 ppm.[9] A similar analysis can be performed for 8 and the ^{13}C NMR and other spectra are consistent with the proposed structures

An addition-cleavage mechanism seems to us hard put to explain 7 and 8 and we think it best abandoned. In its place we suggest a concerted, two-bond "pluck" mechanism in which the central and one side bond of the bicyclobutane are simultaneously[10] cleaved. Striking as this process appears, good analogy exists in the intramolecular fragmentation of cyclopropylcarbenes. This is known to be a concerted[10] reaction in which the stereochemical relationship of the groups attached to the cyclopropane ring is preserved in the fragment olefin.[11] Tests for this mechanism, though hard, are available and are being pursued, as is the question of the relation between this reaction and other cleavages of exceptionally strained molecules.[12-14]



REFERENCES AND NOTES

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(2) Portions of this work are taken from the A.B. Thesis of GBM, Princeton University, 1981. We thank Ms. Evelyn Hillhouse for experimental assistance.

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(7) The formation of *p*-xylene from 4,4-dimethylcyclohexadienylidene may be such an example. It is not clear, however, whether the reacting spin state in this reaction is singlet or triplet. See: T. E. Berdick, R. H. Levin, A. D. Wolf, and M. Jones, Jr., *J. Am. Chem. Soc.*, 95, 5087 (1973).

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(10) We use the word in the operational sense, as one might when referring to the "simultaneous" formation of two new bonds during the addition of a singlet carbene to an olefin. Theoretical treatments present no such simple picture, although the intermediates they postulate are committed to closing on formation. See: R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Am. Chem. Soc.*, 93, 6188 (1971); N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, 94, 9095 (1972).

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