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THE SYNTHESIS AND SOME REACTIONS OF 1,2,2-TRIMETHYLBICYCLOBUTANE[1a]

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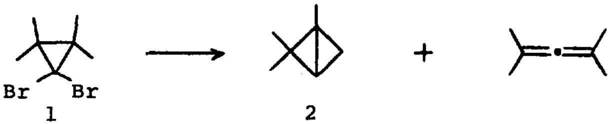
gem-Dibromocyclopropanes react with methyllithium to generate carbenoid intermediates which undergo subsequent reaction in a manner determined by the kind and number of substituents. The dibromocarbene adducts of mono-, di-, and tri-alkyl substituted acyclic olefins give allenes in excellent yields as do the adducts of alicyclic olefins[2] unless a highly strained allene would be formed, in which case products resulting from intramolecular insertion or a competing carbene reaction are observed.[3] Thus while the dibromocarbene adduct of cyclohexene gives a bicyclobutane (tricyclo[4.1.0.$0^{2,7}$]heptane) as a major product,[3a] the dibromocarbene adduct of trimethylethylene gives only trimethylallene[2d] (we find > 98%).

In sharp contrast, we have found that in general the dibromocarbene adducts of tetraalkyl-substituted olefins give bicyclobutanes, not allenes, as the major products. Several examples and a possible rationalization are presented in the accompanying paper.[4] Here we report as a prototype the behavior of the simplest case, the dibromocarbene adduct of tetramethylethylene 1, a system which we have examined in some detail.

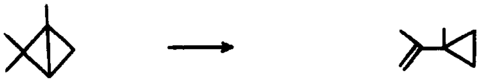
Dibromide 1 reacts with methyllithium in ether at 0° to give quantitatively



1 2

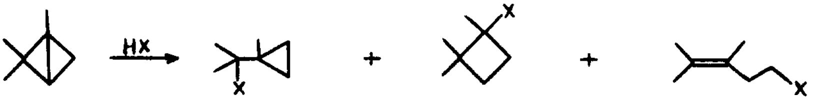
(100 ± 2% by glc) a mixture of almost pure 1,2,2-trimethylbicyclobutane (2) along with a small amount (*ca*. 2%) of tetramethylallene. Pure 2 has been

obtained by distillation through a Teflon spinning-band column.[5,6] The structure of 2 is clearly established by its spectral[6] and chemical properties. Compound 2 is indefinitely stable in the absence of acidic surfaces[7] or impurities which cause isomerization to mainly olefin 3. The latter compound was isolated in good yield from the treatment of 1 with methyllithium by Skattebøl,[2d] who suggested that 2 was an (unstable) intermediate formed by insertion of an intermediate cyclopropylidene into one of the methyl groups.[8] Thus 2 is readily isomerized by magnesium bromide in ether to 3 (along with ca. 4% of an isomer[9]).



2 3

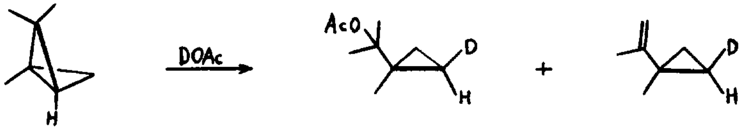
Carboxylic acids and water (with acid catalysis) add to 2 to give mainly, but not exclusively, the cyclopropylcarbinyl derivatives 4. Thus addition of acetic acid to 2 in pentane at 0° gave 12% 3 and a mixture (88%) comprised of 93% 4a, 1% 5a and 6% 6a. Addition of acetic acid-O-d to 2 has established that



2 4 5 6

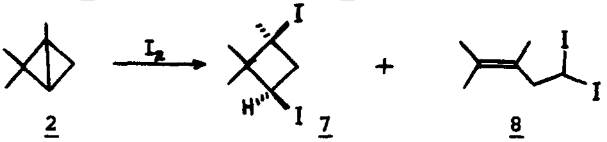
a, x = OAc; b, x = p-nitrobenzoate; c, x = OH

both 3 and 5 are formed with the deuterium oriented cis to the acetoxyisopropyl and isopropenyl groups, assignments based on the nmr spectra of the deuterated

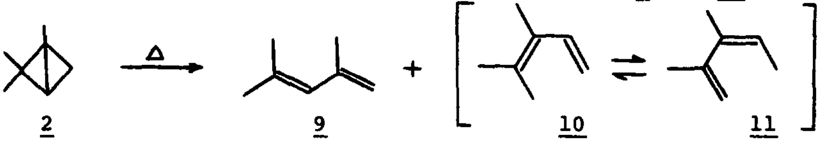


compounds and that of the deuterated 1-methylcyclopropane carboxylic acid obtained by pyrolysis of 4a to 3 followed by ozonolysis and hypochlorite oxidation. This case thus provides another clear indication that the addition of a proton (deuteron) to a bicyclobutane occurs with retention of configuration.[10]

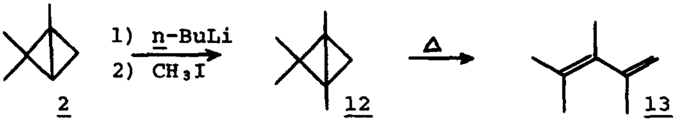
Iodine in carbon tetrachloride adds rapidly to 2 to give a 55:45 mixture (70-80% yield) of the cis-diiodocyclobutane 7 and the homoallylic diiodide 8 (the balance of 2 is isomerized to 3 and the minor isomer[8]).



Pyrolysis of 2 has been studied over the range of 280-400°. Low conversion at the lower temperatures gives the expected dienes 9 and 10. Longer contact



times or especially higher temperatures result in the formation of increasing amounts of 11, shown to result from 1,5-sigmatropic rearrangement of 10 (at 400° the equilibrium ratio is 10:11 = 55:45). The ratio of 9:10 initially formed (i.e., 9:10 + 11) is *ca*. 48:52 and virtually independent of temperature. 1,2,2,3-Tetramethylbicyclobutane 12, obtained (in *ca*. 90% yield) by metallation of 2 with *n*-butyllithium – tetramethylethylenediamine followed by alkylation with methyl iodide, undergoes pyrolysis over a comparable temperature range to give only 2,3,4-trimethyl-1,3-pentadiene (13). In the case of both 13 and 9,



1,5-sigmatropic rearrangements no doubt occur, but in each case the starting material would be regenerated (thermal degeneracy).

REFERENCES

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(5) All new compounds have been characterized by ir, nmr, and mass spectra and by elemental analysis.

(6) Bp 84°, n^{25} D 1.4185. Nmr (CCl_4) δ: 0.78 s, *endo*-2-CH_3 superimposed on a broader signal from the 3-H (confirmed by replacement of the 3-H by deuteration, *2* plus *n*-butyllithium, then D_2O); 1.08 s, *exo*-2-CH_3; 1.18 br s *endo* -4H; 1.40 app. q, *exo* -4H; 1.47 s (very fine splitting), 1-CH_3. Mass spec. m/e 96 (M^+).

(7) We wash all glassware thoroughly with potassium hydroxide in methanol and conduct distillations over potassium carbonate.

(8) Our initial isolation of *4* was communicated to Dr. Skattebøl while his report[2d] on the isolation of *5* was in press. Subsequently Dr. Skattebøl has also isolated *4* and studied a number of its reactions.

(9) This compound probably is 2,3,3-trimethylcyclobutene.

(10) For other examples see (a) W. G. Dauben and F. G. Wiley, *Tetrahedron Lett.*, 893 (1962); W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, *9*, 539 (1964); (b) E. P. Blanchard, Jr. and A. Cairncross, *J. Amer. Chem. Soc.*, *88*, 487 (1966); (c) K. B. Wiberg and G. Szeimies, *ibid.*, *92*, 571 (1970).