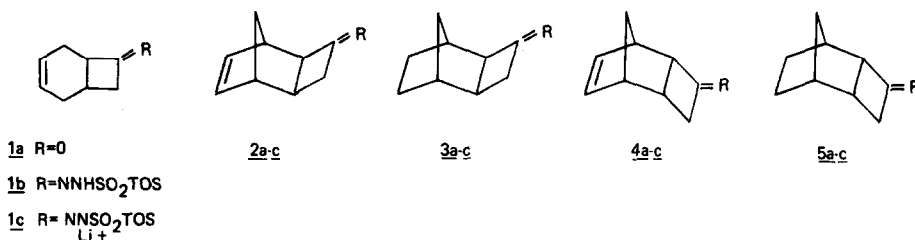


REACTIONS OF POLYCYCLIC CYCLOBUTYL CARBENES: METHYLENE CYCLOPROPANE DERIVATIVES

R. D. Miller and D. L. Dolce
IBM Research Laboratory San Jose, California

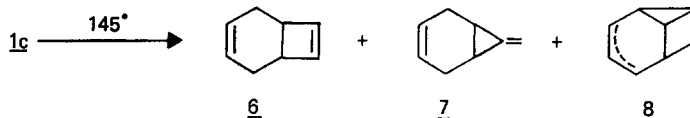
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As part of a general program to examine the chemistry of a number of polycyclic cyclobutanones¹ and their simple derivatives, we have investigated the behavior of a number of polycyclic cyclobutyl carbenes produced by the pyrolysis of the corresponding lithium salts 1c-5c. We were interested in the effect of the additional fused ring, in particular when this ring incorporated added geometric strain, on the available reaction pathways of cyclobutyl carbenes.² Additionally, the derivatives 1c-5c seemed to be interesting starting materials for the preparation of fused ring methylene cyclopropanes to serve as thermal precursors to cyclic trimethylene methane diradicals at moderate temperatures and in the case of the unsaturated derivatives as potential sources of methylene cyclopropene via a retro Diels Alder reaction under conditions of flash vacuum pyrolysis. A very recent report concerning the preparation and thermal rearrangement of 3-isopropylidenetricyclo[3.2.1.0^{2,4}]oct-6-ene prompts us to report our preliminary results.³



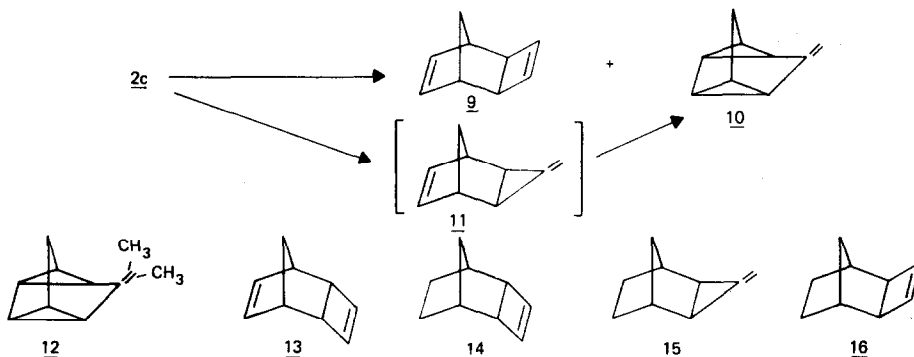
The pyrolysis of 1c produced a mixture (20%) of four major C₈H₁₀ hydrocarbons. Three of the products were AgNO₃ soluble and were subsequently recovered by treatment with NH₄OH at 0°. The minor product (3%) of the AgNO₃ soluble fraction was identified by its spectral data as bicyclo[4.2.0]octa-3,7-diene.⁴ The second product (9%) in this fraction, which was the major product of the pyrolysis was identified by its spectral data as the desired methylene cyclopropane derivative, 7: IR (CCl₄) 3070, 3035, 2900, 2945, 1780, 1755,⁵ 1660, 1440, 1295, 1213, 1140, 985, 890 and 712cm⁻¹; NMR (CCl₄) τ 4.68 (br s, 1/2wd 4Hz, 2H) 4.77 (t, J=2Hz, 2H), 7.80 (br s, 1/2wd 5Hz, 4H) and 8.48 (m, 1/2wd 6Hz, 2H). Controlled hydrogenation of 7 (PtO₂..

hexane, 25°) produced endo-7-methylnorcarane⁶ (>80%). The cyclopropane derivative, 7, showed considerable thermal stability and could be recovered unchanged after heating in a sealed tube (210°) for two hours. The identification of the third component (2%) of the silver nitrate soluble fraction was complicated by inability to obtain the material free of contaminants and its tendency to polymerize. An additional C₈H₁₀ material (5%) was isolated from the AgNO₃ insoluble fraction. The spectral data for this material is as follows: IR (CCl₄) 3035, 2960, 2920, 2880, 2830, 1640, 1430, 1268, 1050, 986, 975, 875 and 720cm⁻¹; NMR (CCl₄) τ 4.10-4.58 (m, 2H) and 7.33-8.98 (complex multiplet, 8H); CMR⁷ (CDCl₃) δ 125.145, 124.002, 28.721, 26.763, 25.678, 20.362, 15.960 and 14.65. The UV spectrum (C₆H₁₄) showed strong end absorption with no maximum λ >2100 (ε₂₁₀₀=3900). Exhaustive catalytic hydrogenation (10% Pd/C, hexane) resulted in the uptake of two moles of hydrogen and the formation of bicyclo[3.2.1]octane in 88% yield. This data is basically consistent with either of the double bond isomers of 8. Tricyclo[3.2.1.0^{7,8}]oct-2-ene however seems more reasonable on the basis of the strong end absorption in the UV and on mechanistic grounds, since it represents intramolecular insertion of the cyclobutyl carbene into an adjacent carbon hydrogen bond which has some literature precedent.⁸



To investigate the effect of strain in the peripheral fused ring on product distribution and at the same time provide increased ground state strain to facilitate thermal rearrangements of the expected methylene cyclopropane derivative, the pyrolysis of 2c was carried out at 145°. The crude pyrolysate contained two major C₉H₁₀ hydrocarbons. The spectral data of the lower boiling component (3%) was as follows: IR (CCl₄) 3100, 3060, 3040, 2970, 2940, 1550, 1450, 1320, 1285, 1255, 1250, 1180, 710 and 690cm⁻¹; NMR (CCl₄) τ 3.85 (s, 2H), 3.99 (m, 2H), 7.68 (s, 1/2wd 3Hz, 2H) and 8.62 (ABq, J=9Hz, 2H). This data is consistent with the assignment of structure 9. The appearance of the cyclobutene methine protons as a singlet confirms the exo geometry. The higher boiling material (6%) which was only partially removed by the AgNO₃ was identified as 10, from its spectral data and independent synthesis.⁹ A most likely precursor to 10 would be the methylene cyclopropane 11 which could then undergo subsequent thermal cycloaddition under the reaction conditions. The postulated intermediacy of 11 in the pyrolysis is greatly strengthened by the observation of Block and coworkers³ who

found that 3-isopropylidenebicyclo[3.2.1.0^{2,4}]oct-6-ene is rapidly converted to 12 upon heating to 180°.



If 11 is truly an intermediate in the pyrolysis of 2c, the formation of 10 could be rationalized either as an intramolecular trapping¹⁰ of the cyclic trimethylene methane diradical produced from 11, or alternatively as a concerted $\pi 2s + \sigma 2s$ symmetry forbidden but energetically allowed cycloaddition.¹¹ To look for a possible stereoelectronic effect on the reaction pathways, the pyrolysis of the corresponding endo derivative 4c was investigated under identical conditions. At 145°, 4c yielded only 13¹² and 10 in yields of 3% and 9% respectively. In order to assure ourselves that a methylene cyclopropane derivative can in fact be produced from a cyclobutyl carbene fused to a strained bicyclic system, the saturated derivative 5c was examined. The pyrolysis of 5c led to two major and difficultly separable C₉H₁₂ hydrocarbons. The minor component (3-4%) was the expected cyclobutene, 14: IR (CCl₄) 3100, 3040, 2940, 2860, 1465, 1445, 1160, 1110, 925 and 695cm⁻¹; NMR (CCl₄) τ 3.78 (s, 2H), 7.16 (d, J=3.8Hz, 2H), 7.81 (m, 2H) and 8.33-8.72 (m, 6H dominated by two broad singlets at 8.49 and 8.69). The major component (8-10%) had IR bands at 3060, 2950, 2870, 1763, 1740, 1450, 1295, 1065, 975, 880 and 850cm⁻¹. The NMR (CCl₄) reflected molecular symmetry with absorptions at 4.87 (t, J=1.3Hz, 2H), 7.65 (m, 1/2wd 5Hz, 2H) 8.35-8.73 (m, 4H), 8.52 (weakly split broad singlet, 1/2wd 3Hz, 2H) and 9.15 (ABq, J=9.5Hz, 2H). This data is consistent with the expected methylene cyclopropane derivative, however the stereochemistry of the three-membered ring requires further discussion. Decoupling showed that the broadened singlet at 8.52 τ was due to the methine protons of the cyclopropane group. Under ordinary circumstances the absence of a 3-4Hz splitting of these by the bridgehead protons would imply an exo arrangement for the three-membered ring.¹³ However the geometric distortion in this system is enough to create some doubt concerning the validity of geometric assignment based

only on coupling constants. For this reason, the exo derivative 3c was prepared and pyrolyzed. Again two major C_9H_{12} hydrocarbons were produced in 7 and 8% respectively. The lower boiling material was identified as the cyclobutene, 16: IR (CCl_4) 3115, 3040, 2950, 2875, 1550, 1450, 1325, 1300, 840 and $700cm^{-1}$; NMR (CCl_4) 4.20 (s, 2H), 3.56 (s, 1/2wd=2.5Hz, 2H), 8.12 (m, 2H), 8.38-8.60 (m, 3H) and 8.92-9.18 (m, 3H). The second and major product was identical in every respect to the methylene cyclopropane produced from 5c. It now seems reasonable to assume that the geometry of the common product, 15, is the thermodynamically more stable exo derivative. Hence under the reaction conditions while the cyclobutene derivatives 14 and 16 have retained the geometry of the starting material, the methylene cyclopropane has been equilibrated.

It seems now that fused ring and polycyclic methylene cyclopropanes are accessible from cyclobutyl carbene contractions even in cases where the fusion is to a strained bicyclic system. However in cases of high peripheral strain one must expect stereochemical equilibration and in some cases complications due to internal cycloaddition.

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