

A THERMAL CYCLOPROPYLIDENECYCLOPROPANE-
METHYLENESPIROPENTANE REARRANGEMENT^{1a}

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Considerable interest has recently been focused upon the thermal behavior of methylene-cyclopropanes.² The present report describes some studies on compounds in which this reactive moiety is incorporated into a more complex small-ring system.

Reaction of alkenylidenecyclopropane 1³ with methylene iodide and zinc-copper couple led to cyclopropylidenecyclopropane 2 in good yield.⁴ Compound 2 displays a two-proton singlet at τ 9.08 and three equivalent singlets totaling 18 protons at τ 8.87, 8.86, and 8.84 in its nmr spectrum in agreement with the assigned structure. Predominate formation of this material over its isomer 3 is dictated by both steric and electronic⁵ factors.⁶

Pyrolysis of 2 in a flow system at 400° (0.2 mm) effected conversion to 2 (4%), 3 (9%), and methylenespiropentane 4 (87%). A comparison sample of 4 was produced by Simmons-Smith reaction of dimethylenecyclopropane 5.³ Compound 4 shows a weak methylenecyclopropane band at 5.55 μ in the infrared,⁷ and its 100 MHz nmr spectrum displays a two-proton AB pattern centered at τ 9.38 ($\Delta\nu = 10.3$ Hz, $J = 4.0$ Hz) in addition to six distinct methyl singlets at τ 9.01, 8.95, 8.93, 8.91, 8.44, and 8.34.

Separate reaction of methylenespiropentane 4 under the above conditions did not promote detectable reversal to 2, but at higher temperature (510°) this material was converted to a mixture of 37% 4, 31% of triene 6, 13% *p*-xylene, and 5% *o*-xylene. Isomer 3 and, of course, 2 gave similar results. At still more elevated temperatures the xylenes were the only major products, and it was independently demonstrated that triene 6 also gave the aromatic compounds cleanly. Triene 6 [ir 3.20, 6.12, 7.3, 9.2, and 11.2 μ ; 100 MHz nmr τ 8.51 (s, 3), 8.44 (s, 3), 8.36 (m, 9), 8.31 (s, 3), 5.37 (m, 1), 5.07 (m, 1); uv max (hexane) 216 m μ (ϵ 12,500)] was identical with an authentic sample prepared from 7³ by methyl lithium addition, acid dehydration of the resulting alcohol, and thermal equilibration of the resulting triene

mixture.

Dolbier has examined the parent methylenespiropentane which was found to isomerize to 1,2-dimethylenecyclobutane in the major thermal reaction.⁸ This observation prompted synthesis and investigation of the analogous dimethylenecyclobutane 8 which would be expected in the present system. The preparation of 8 was accomplished by methyllithium addition to ketone 9⁸ followed by phosphorous oxychloride dehydration of the resulting alcohol. Compound 8 shows: ir 3.12, 6.0, 6.12, and 11.6 μ ; 100 MHz nmr τ 8.98 (s, 6), 8.87 (s, 6), 8.29 (s, 3), 8.25 (s, 3), 5.36 (m, 1), and 5.19 (m, 1); uv max (hexane) 248 m μ (ϵ 14,300). Pyrolysis of 8 at 460° gave 6 (72%) and 8 (4%). This experiment explains the absence of 8 in the pyrolysis products of 2, 3, and 4, since this material clearly would not have accumulated in the reactions described above even if it were an important product.

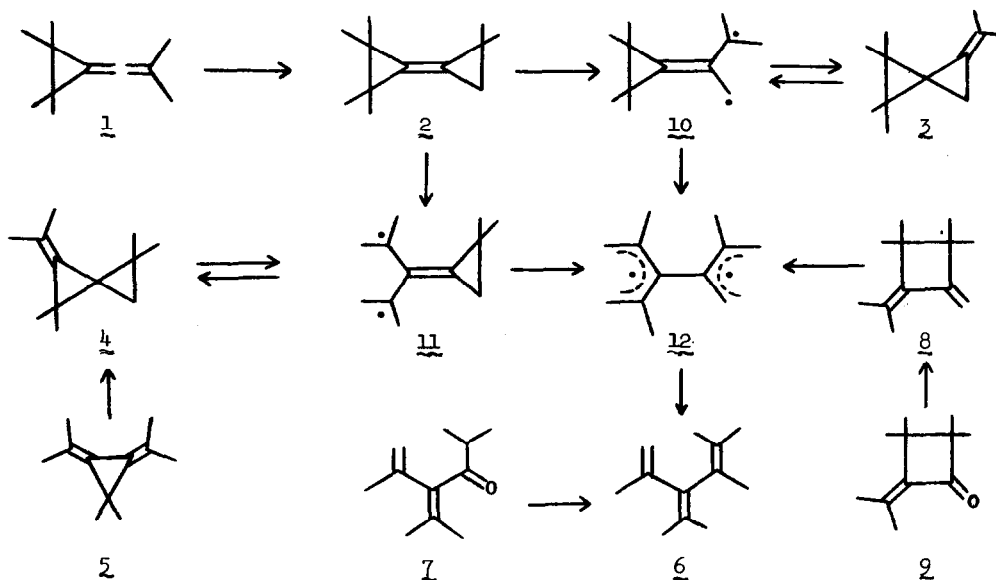
The results of this study are nicely accommodated by a mechanistic scheme based on trimethylenemethane-type intermediates as summarized in the chart. Thus, the transformations of even these highly perturbed methylenecyclopropanes are subject to rational analysis. The cyclopropylidenecyclopropane 2 is converted to its methylenespiropentane isomers 3 and 4 via the respective intermediates 10 and 11. No back reaction is observed in accord with the anticipated lower thermodynamic stability of 2. The preference for products derived from 11 probably reflects the greater stabilization by alkyl groups and relief of nonbonded interactions which are influential in the transition state leading to this diradical intermediate. There is no evidence for appreciable equilibration of 2 and 3 in support of this kinetic argument. A competing reaction branch from the trimethylenemethane intermediates 10 and 11 is rearrangement to the interesting bis-allyl diradical 12, but this isomerization has a relatively high activation energy and is only important at elevated temperatures. In essence, this conversion is a cyclopropyl radical to allyl radical rearrangement⁹ which is known to have an appreciable activation barrier.¹⁰ Diradical 12 leads readily to triene 6 by disproportionation through a favorable six-center hydrogen transfer. Intermediate 12 can also be approached by thermal bond homolysis of dimethylenecyclobutane 8. This is probably a reversible process, but the severe nonbonded repulsion in 8 and the availability of alternate reaction pathways for 12 account for the difference between the parent system⁸ and the present methylated derivatives.

Finally, the formation of the xylenes is attributed to further, rather complicated, but understandable processes emanating from triene 6. Elaboration on this topic, however, is

reserved for a more appropriate time.

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Chart



References

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