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METHYLENESPIROPENTANE

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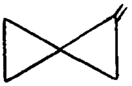
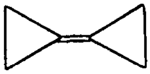
In connection with our recent studies on the thermal degenerate rearrangement of 1,2-bis-methylenecyclobutane (1), we believed it of interest to investigate the thermal rearrangements of methylenespiropentane, I, and bis-cyclopropylidene (2), II, with our eventual goal the definition of the energy surface which relates these compounds to 1,2-bis-methylenecyclobutane and allene, in much the same way as spiropentane, methylenecyclobutane and the pair of molecules, allene and ethylene, have been related (3).



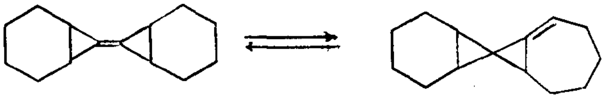
I



II

Methylenespiropentane was synthesized from diethyl isopropylidene malonate (4) via the following steps: 1: allylic bromination with N-bromosuccinimde; 2: addition to potassium t-butoxide in t-butyl alcohol to give diethyl 2-methylene-cyclopropane-1,1-dicarboxylate (5); 3: reduction with $LiAlH_4$ in ether (6); 4: conversion of the diol to the bis-toluene sulfonate ester by treatment with toluenesulfonylchloride in pyridine; and 5: treatment of the crude ditosylate with zinc in the presence of tetrsodium ethylenediamine tetraacetate (7) to give methylenespiropentane (8) broad singlets in the NMR at 1.02 (2H) and 1.12 (2H), an ill defined multiplet at 1.33 (2H), a triplet (J=2 1/2 cps) at 5.08 (1H) and a broad singlet at 5.21 (1H) ppm; bands in the ir (gas, 39 mm.) at 3081 (s), 3010 (s), 1797, 1743, 1443 (w), 1360 (w), 1165, 1084, 1005 and 881 (s) cm^{-1}; and a mass spectrum with parent peak at m/e 80.

Since bis-norcarylidene, III, thermally equilibrates with IV upon heating at 210°, (9,10) one had dared hope that I would yield some II upon similar



III IV

heating; however, I was recovered unchanged after 20 hours at 209 ± 2°. This is an indication that *bis*-cyclopylidene is significantly less stable than methylenespiropentane.

Rearrangement of I could be effected, however, by heating to temperatures above 300 . After 10 hours at 300 ± 2°, approximately 8% of I had been converted to two products, XI and VIII, in the ratio of 1:7. Heating to 320 ± 2° for 20 hours led to a mixture of isomers containing 60.6% I, 19.8% XI, 15.8% VIII and 3.8% of a very volatile product, probably allene (11).

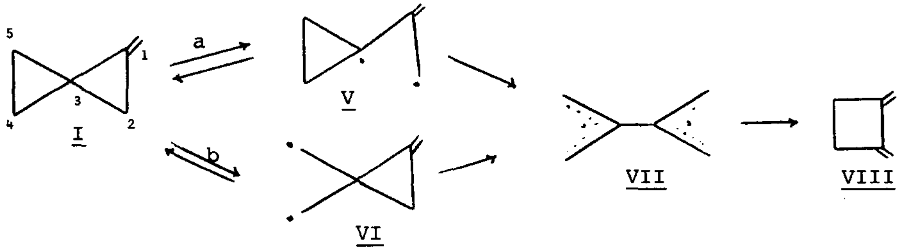
The products were characterized by their NMR and infrared spectra. XI showed two pentuplets (J=2 cps.) of equal intensity in the NMR at 3.28 and 4.85 ppm. and had, *inter alia*, bands in the ir (gas, 12 mm.) at 3093, 3002, 2930, 1655 and 899 (s) cm^{-1}. VIII showed three broad singlets in the NMR at 2.58, 4.64 and 5.07 ppm. with relative intensities of 2:1:1, and had bands, *inter alia*, in the ir (gas, 10 mm.) at 3084, 2984, 2944, 1750, 1650, 1415, 1240 and 885 (s) cm^{-1}.

The spectra of XI were consistent with it being 1,3-*bis*-methylenecyclobutane (12), and those of VIII were identical to spectra of an authentic sample of 1,2-*bis*-methylenecyclobutane.

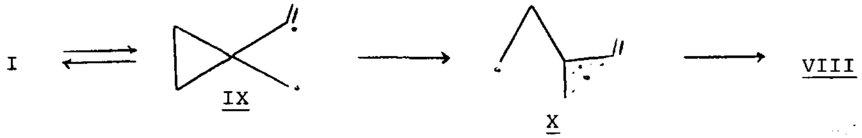
1,2-*Bis*-methylenecyclobutane has been shown to dimerize in the gas phase, even at lower pressures and temperatures than those used in these pyrolyses (1). The recovery of volatile products in the higher temperature pyrolysis, run at 23 mm., was only 40%. Thus dimerization VIII apparently accounts for its relative dimunition in this pyrolysis.

The elegant work of Burkhardt (and Swinehart) (13) as well as that of Doering and Gilbert (3) strongly indicates that rearrangements of the spiropentane system involve diradical intermediates rather than concerted processes. In a like manner, the rearrangement of methylenespiropentane is most fruitfully discussed in terms of diradicals.

Since C_2-C_3 cleavage should occur quite readily at temperatures as low as



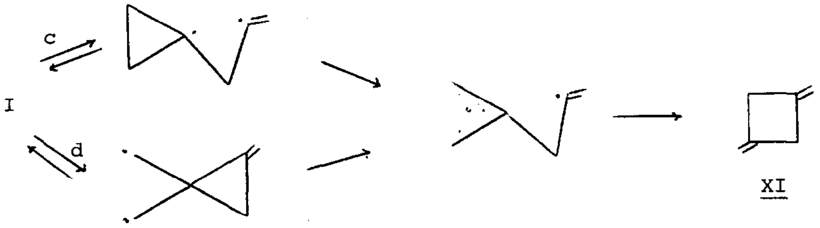
200°(14), it seems a logical conclusion that, at 300°, methylenespiropentane is in equilibrium with a trimethylenemethane type of diradical, V. Therefore a logical route to VIII, would be via the bis-allyl diradical, VII, obtained by C_4-C_5 cleavage of V (path a). In spite of the equilibrium between I and V, one cannot rule out at this time the possibility that the order of these two bond cleavages may be reversed (path b). Still another possibility of initial C_1-C_2 followed by C_3-C_4 cleavage (path c) is probably less likely because of the



relative stability of the hypothetical intermediates, IX and X.

A surprise, of course, is the appearance of 1,3-bis-methylenecyclobutane as a product. Allene dimerization was ruled out as a source of the products (15). Therefore, 1,3-bis-methylenecyclobutane may only be explained by allowing that a process involving an intermediate vinyl radical is occurring.

The most likely pathways for this process are c and d, with their only difference being the order of bond cleavages.



We hope that further experiments involving verification of preequilibria and determination of activation parameters for the parent hydrocarbon as well as various substituted methylenespiropentanes will shed light on the chemistry of this system.

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9. W. R. Dolbier, unpublished results
10. All pyrolyses in this work were carried out in a 566 cc. pyrolysis tube sealed under vacuum, and heated in a stainless steel tube furnace.
11. Allene was characterized only by simultaneous gas chromatographic injection of an authentic sample with the pyrolysis mixture.
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15. Allene was shown not to dimerize significantly under the pyrolysis conditions, even at pressures as high as 30 mm.