Tetrahedron Letters No. 33, pp 2813 - 2816, 1974. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND VALENCE ISOMERIZATIONS OF 1,1'-TETRAMETHYLENEBICYCLOPROPENYL

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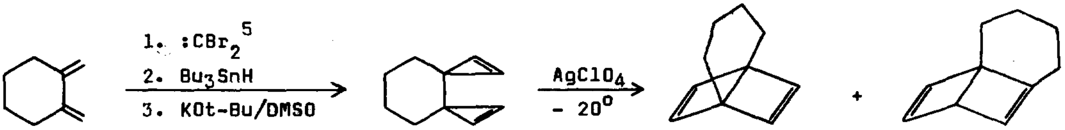
(Received in UK 21 June 1974; accepted for publication 26 June 1974)

In the study of the valence isomerizations of 1,1'-dimethylbicyclopropenyl[1] we encountered results[2] and problems[3] which made it desirable to investigate the analogous reactions of bicyclopropenyls which are connected between positions 1 and 1' and thus sterically and rotationally restrained. One could expect not only to resolve certain mechanistic ambiguities, but also to obtain novel isomerization products with their own intrinsic interest. In this communication we report preliminary results obtained with 1,1'-tetramethylenebicyclopropenyl (dispiro[2.0.2.4]deca-1,5-diene, I).

The synthesis of I[*] [NMR ($CDCl_3$): δ 7.10 (s, 4H), 1.57 (m, 8H); IR (neat): 1620 cm^{-1} (C=C)] from 1,2-dimethylenecyclohexane[4] was straightforward and analogous to that of 1,1'-dimethylbicyclopropenyl[1] (10% overall yield).



I II III

On treatment with $AgClO_4$ in different solvents at - 20° C I yielded the two expected[2] Dewar benzenes II[*] [NMR ($CDCl_3$): δ 6.50 (s, 4H, =CH), 1.91 (m, 4H), 1.39 (m, 4H); IR (neat): 1533 cm^{-1} (C=C)] and III [NMR ($CDCl_3$, after subtraction of the signals of II): δ 6.65, 6.53 (AB-system, J = 3 Hz, CH=CH), 5.87 (broad s, 1H, =CH), 3.64 (broad s, 1H, bridgehead proton)]. The ratio of II and III depended on the solvent used for the isomerization (Table 1).

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[*] The compound gave an elemental analysis and/or a high resolution mass spectrum in agreement with its assigned structure.

The preferred formation of III in less polar solvents may be explained on the basis of the mechanism proposed by Weiβ and Andrae[6] by increasing energy content and reactivity of the intermediate cyclobutenylcarbonium ion.

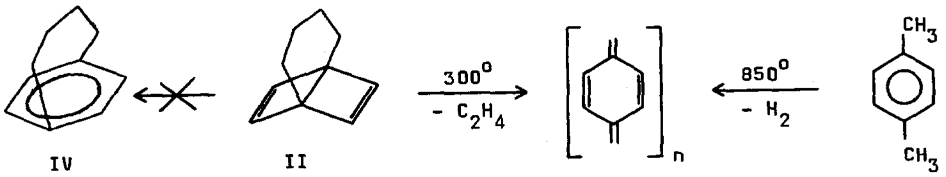
Table 1

solvent :	$CDCl_3$	DME	CD_3CN	CH_3OH
ratio II : III[a]:	0.20	0.45	0.70	0.78[b]

a. determined from NMR after rearrangement of III to tetralin,

b. no CH_3O-containing products were observed (NMR).

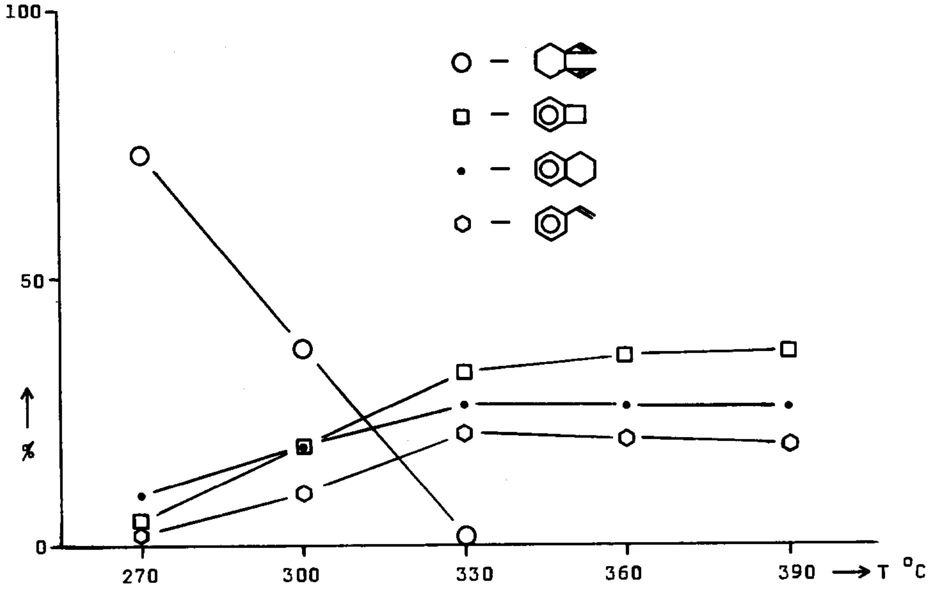
III was thermally unstable ($t_{1/2}$ = 58 min at 20° C) and rearranged to tetralin quantitatively. It could for this reason not be isolated in pure form. II, on the other hand, was thermally unusually stable ($t_{1/2}$ = 26 min at 140° C). Contrary to its analogue, 1,4-dimethyl(Dewar benzene)[2], it could not be aromatized to the highly strained IV[7]; attempts to isolate IV after pyrolysis in a flow system[8] at 300° C (residence time ca. 0.5 sec) led to poly-p-xylylene[9] (identified by comparison of its IR spectrum and elemental analysis with those of an authentic sample) as the only product.

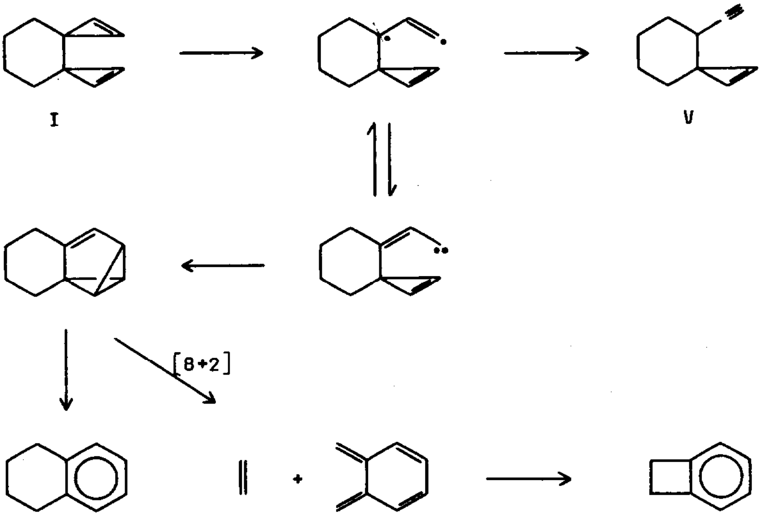


A similar fragmentation is less likely for 1,4-polymethylene(Dewar benzenes) with an uneven number of carbon atoms; experiments with the tri- and pentamethylene derivatives are in progress.

The thermal behaviour of I was investigated in order to compare it with that of II; however, the results were largely different. Depending on the reaction temperature in the flow system, tetralin, styrene and benzocyclobutene were obtained (Fig. 1), besides six minor peaks in the GLC, one of which was tentatively identified as V [IR: 3315, 2105, 1630 cm^{-1}]. The total recovery of products was close to 100%.

Figure 1





It is plausible to rationalize the formation of these products by first postulating bond breakage of a cyclopropene ring to form a diradical[10] or vinylcarbene[11] which can rearrange to V. However this seems to be a minor pathway; the main reaction to tetralin and benzocyclobutene will proceed via a benzvalene (or equivalent diradicals). Fragmentation routes to styrene can be conceived on paper, but more experimental evidence is needed to make a reasonable decision.

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