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1,4-TRIMETHYLENE(DEWAR BENZENE)

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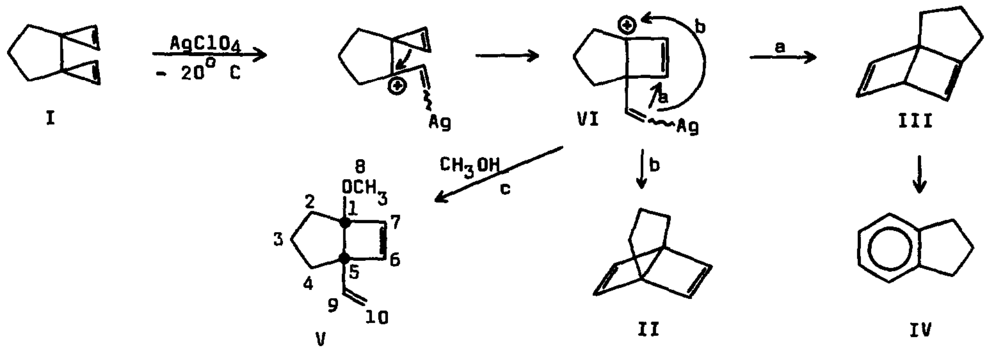
In the course of our investigations of 1,1'-polymethylenebicyclopropenyls[1] we found that silver ion promoted valence isomerization of 1,1'-tetramethylenebicyclopropenyl led to 1,4-tetramethylene(Dewar benzene). Attempted aromatization of this interesting compound[1,2] to [4]-paracyclophane was thwarted by its ready fragmentation on pyrolysis. This escape reaction being impossible with uneven polymethylene(Dewar benzenes), it was of interest to study 1,1'-trimethylenebicyclopropenyl (I) and 1,4-trimethylene(Dewar benzene) (II), even though aromatization of the latter to [3]-paracyclophane could be expected to be prohibited by excessive strain. In fact, II turned out to be an extraordinarily stable compound, while on the other hand evidence was obtained for the mechanism of the aforementioned silver ion promoted valence isomerizations.

I[3] [NMR ($CDCl_3$): δ 6.99 (s, 4H), 1.67 (m, 6H); IR (neat): 1630 cm^{-1}] was obtained from 1,2-dimethylenecyclopentane[4] in 21% overall yield in complete analogy to its tetramethylene homolog[1]. When I was treated with $AgClO_4$ at - 20° C, II[3] was the only detectable Dewar benzene [NMR ($CDCl_3$): δ 6.57 (s, 4H), 2.14 (quintet, J = 6 Hz, 2H), 1.58 (t, J = 6 Hz, 4H); IR (neat): 1530 cm^{-1}]; the expected[1,5] III, being still more strained than 1,2-tetramethylene(Dewar benzene)[1], apparently aromatized to indane (IV) even at low temperatures. In general, II and IV were the only products observed; their ratio II : IV was solvent dependent ($CDCl_3$: 1.5; CD_3COCD_3 : 2.7; CD_3CN : 4.8; CH_3OH : 5.1). In CH_3OH, a third product V was found; the yield of the three products was nearly quantitative (ratio II : IV : V = 36 : 7 : 57). V[3] was identified as 1-methoxy-5-vinylbicyclo[3.2.0]-hept-6-ene by its spectra[6] [^1H NMR ($CDCl_3$): δ 6.08, 6.02 (AB, J = 3 Hz, 2H), 6.03, 5.11, 5.10 (ABC, J = 2, 10, 18 Hz, 3H), 3.31 (s, 3H), 1.46 (m, 6H); ^{13}C-NMR ($CDCl_3$): ppm downfield from TMS (assignment, off resonance multiplicity): 140.5 (C_9, d), 139.4, 135.4 (C_6 and C_7, 2d), 114.2 (C_{10}, t), 94.2 (C_1, s), 63.9 (C_5, s), 53.3 (C_8, q), 31.3 (C_2 and

C$_4$, t), 22.4 (C$_3$, t); IR (neat): 1630 cm^{-1} (CH=CH$_2$), 1560 cm^{-1} (CH=CH)].



V is the first example of a solvent trapped product of a cation of type VI, which has been postulated by Weiss[7] as intermediate in the silver ion catalyzed rearrangement of bicyclopropenyls to Dewar benzenes, and it must be considered as direct evidence for this mechanism[8,9]. Similar products were so far not observed in the rearrangement of other bicyclopropenyls[1,5]. Apparently, developing strain makes intramolecular ring closure (pathway a and b) in VI so unfavourable that solvolysis (pathway c) becomes competitive.

II turned out to be remarkably stable. After flow pyrolysis at 300° the starting materi-

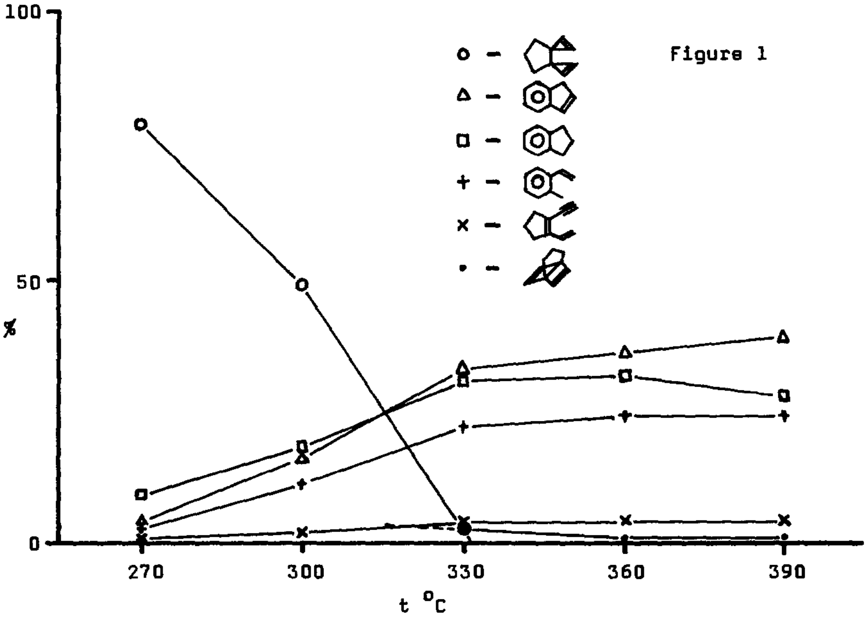
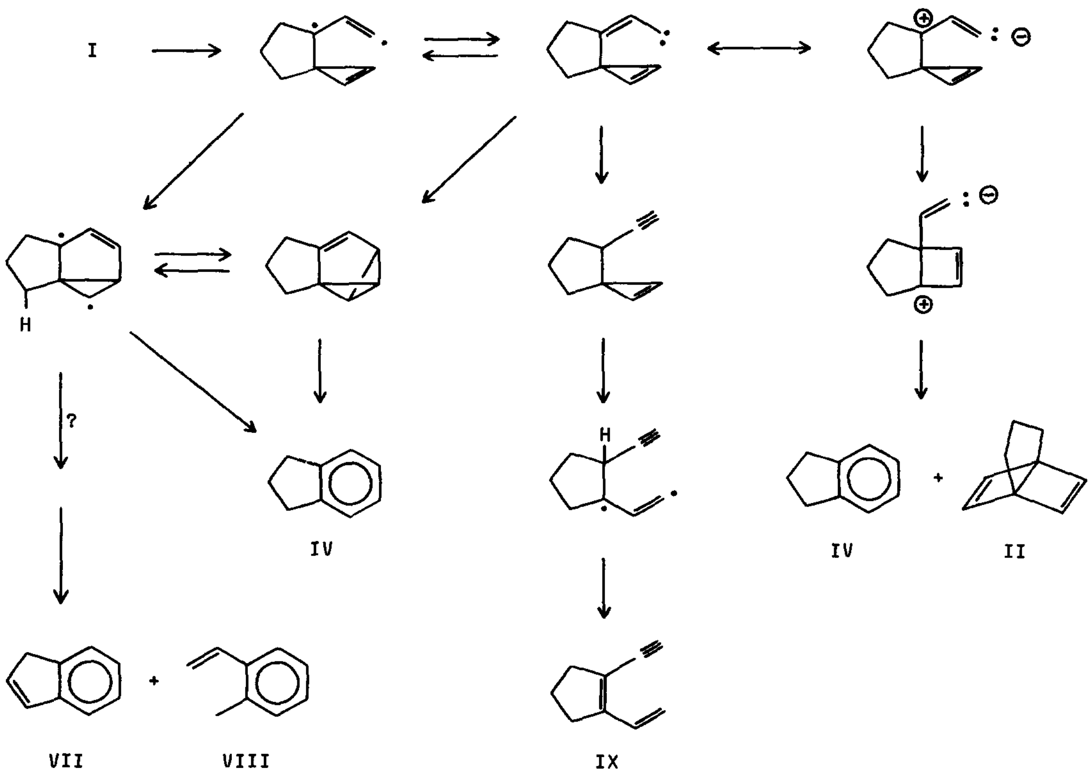


Figure 1

al was recovered quantitatively; no indications for the formation of [3]-paracyclophane were obtained. Interestingly, II was one of the three minor products of the flow pyrolysis[1] of I (contact time ca. 0.5 sec); indene (VII), indane (IV), o-methylstyrene (VIII) and 1-ethenyl-2-ethynyl-cyclopentene (IX) were the main products (see Fig. 1).

Assuming diradical[10] and/or vinylcarbene[11] cleavage of one cyclopropene ring, the formation of II (zwitter ionic intermediate?[7]), IV and IX can be reasonably explained; the formation of VII and VIII probably involves more deepseated rearrangements, the interpretation of which must be rather speculative at this stage.



References

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2. K. Weinges and K. Klessing, Chem. Ber., 107, 1915 (1974).
3. The compound gave a satisfactory high resolution mass spectrum.
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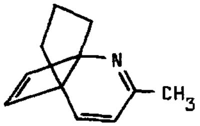
6. We thank Dr. C. Kruk, Universiteit van Amsterdam, for valuable help in the measurement and interpretation of the NMR spectra.
7. R. Weiss and S. Andrae, Angew. Chem., 85, 145 (1973).
8. An analogous dibromovinylcyclobutene has been detected amongst the products of the reaction of Br_2 and a tetraphenylbicyclopropenyl: R. Weiss and H.P. Kempcke, Tetrahedron Letters, 1974, 155.
9. When the reaction was performed in acetonitrile the NMR spectrum of the reaction mixture (vinylic protons at δ 5-6 ppm) and GC-MS (m/e = 159.1046, calc. for $C_{11}H_{13}N$: 159.1048) indicated the presence of an adduct of the presumable structure:



the formation of which may be the consequence of initial nucleophilic attack of acetonitrile on VI (compare pathway c).

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