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STEREOSELECTIVITY IN THE THERMAL REARRANGEMENT OF 3,4-BISTRIMETHYLSILOXY-1,5-HEXADIYNES.

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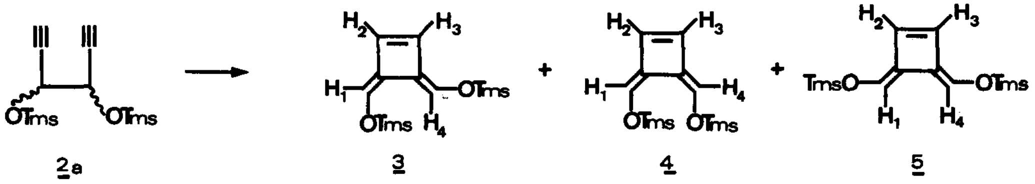
The thermal rearrangement of a number of substitued 1,5-hexadiynes has been reported to lead to bismethylene cyclobutene derivatives [1]. On the other hand, pyrocatechol [2] and 3,5-octadiene-2,7-dione [3] respectively, were obtained in poor yields when 1,5-hexadiyne-3,4-diol 1a and 3,4-dimethyl-1,5-hexadiyne-3,4-diol 1b were pyrolysed. In order to minimize the formation of polymers and fragmentation products [4], and to facilitate the study of the mechanism of these last reactions, we have prepared and submitted to thermolysis the compound 2a

SCHEME I (OTms = O-Si$(CH_3)_3$)



which is the bis-trimethylsilyl ether of 1a.

Meso and racemic diols 1a were separated [5,6] and the bistrimethylsiloxy derivatives 2a prepared by standard method[7].

Thermal rearrangements of 2a were conducted in the gas phase, in a flow system at temperatures ranging from 310° to 500° and at low pressure (20 Torr). The pyrolysis is very clean and almost quantitative recoveries of products are feasible. This reaction leads to the bismethylene cyclobutene derivatives 3, 4, 5. The reaction is highly stereospecific and depends upon the configuration of 2a : so, at a moderate temperature (375°) meso 2a gives 99% of compound 3 ; on the other hand the yield of 3 obtained is less than 1% when the starting compound is racemic 2a at 310°. The stereoselectivity of the reaction is lowered when the temperature is raised.

TABLE I. Effect of Temperature on Product Composition

Isomer	Temperature[a]	Conversion %	Relative per cent of products[a]		
			3	4	5
meso 2a	375°	50	99	1	b
	435°	100	97	3	b
	435°-435°[c]	100	95	5	b
racemic 2a	310°	16	1	51	49
	330°	80	5	50	45
	370°	88	7	52	41
	400°	100	11	53	36
	430°	100	12	56	32
	370-370°[c]	100	7	52	41
	400-500°[c]	100	d	80	20

a) Product distribution determined by the integration of NMR spectrum of ethylenic protons. b) Only traces are formed. c) Pyrolyses were carried out twice at the indicated temperatures. d) The spectrum of 3 is overlapped by that of cleavage products.

It must be noted that the relative amount of the products that are formed is not remarkably modified when the pyrolysis is conducted twice at the same temperature.

The structure of these products has been established by NMR spectroscopy. The rearrangement of 2a having acetylenic hydrogens deuterium labelled permitted us to attribute the signals of cyclobutene and methylene hydrogens without any ambiguity. Only the spectrum of 3 can be easily analysed, it is in conformity with the proposed structure [8]. The signals of 4 and 5 are deduced from the attributions that we proposed for 3.

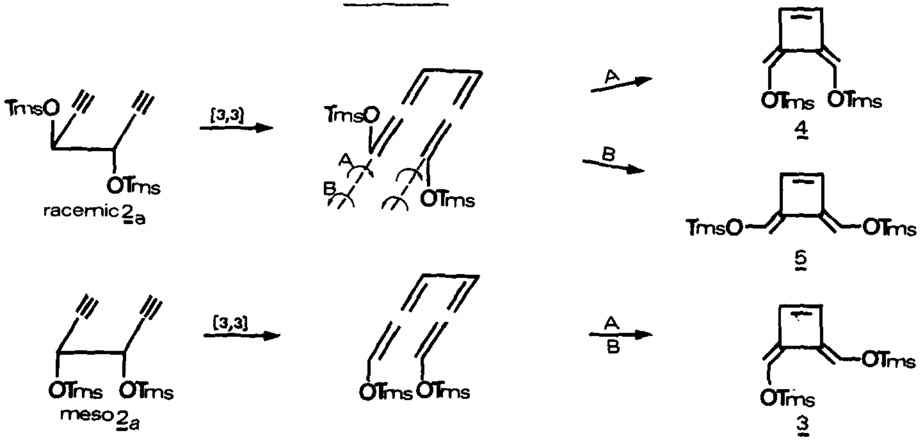
TABLE II. ^{1}H-NMR Parameters of 3, 4, 5 at 60 MHz.

	H_1[a,b]	H_2[a,b]	H_3[a,b]	H_4[a,b]	OTms[a,b]
3[c]	6.24	6.33	6.53	5.96	0.15(s)
4	5.83(m)	6.56(m)	6.56(m)	5.83(m)	0.13(s)
5	5.88(m)	6.22(m)	6.22(m)	5.88(m)	0.13(s)

a) Chemical shifts in p.p.m. for CCl_4 solution with TMS as an internal standard b) s : singlet, m : multiplet. c) J_{12} = 0.8 Hz ; J_{13} = 0 ; J_{14} = 0.3 Hz ; J_{23} = 2.6 Hz ; J_{24} = 0.4 Hz ; J_{34} = 1 Hz.

The thermolysis reported herin at moderate temperature, are best interpreted on the basis of successive concerted mechanisms[9,10]. In the first step, racemic 2a and meso 2a give the corresponding intermediate diallenes by a [3,3] sigmatropic Cope rearrangement. The two conrotatory motions (A and B, Scheme II) lead to the same product 3 in the case of meso 2a and to two different isomers 4 and 5 for racemic 2a. Formation of 4 is noteworthy[11] because i) 4 is the most sterically hindered compound and ii) higher steric compression (between trimethylsiloxy groups) in the transition state leading to 4 relative to 5 was expected.

SCHEME II



This observation coupled with augmentation in the percentage of 4 relative to 5, with increase of the temperature can tentatively be attributed to attractive steric effects between oxygen lone pairs of the trimethylsiloxy groups or between oxygen lone pairs and pi-electrons[12, 13].

If the above hypothesis is valid, it is likely that this attractive interaction is involved in the transition state because 4 is not only the thermodynamic (Table I, at 400-500°) but also the kinetic product (Table I, at 435-435° and 370-370°). As concerns the formation of small quantities of products by a non-concerted reaction, different mechanisms may be envisaged : a biradical, a symmetry non-allowed mechanism, an isomerisation of intermediate diallene ... etc. Further investigation in this direction may finally lead to some specific results, confirming the hypothesis of the attractive steric interaction, besides locating its origin.

REFERENCES

1. a) W.D. HUNTSMAN and H.J. WRISTERS, J.Amer.Chem.Soc., 85, 3308 (1963).
   b) B.A.W. COLLER, M.L. HEFFERMAN and A.J. JONES, Aust.J.Chem., 21, 1807 (1968).
   c) T.J. HENRY and R.G. BERGMAN, J.Am.Chem.Soc., 94, 5103 (1972) and references therein.
2. Unpublished results.
3. J. CHUCHE and N. MANISSE, C.R.Acad.Sci.Paris, 267, 78 (1968).
4. R.W. THIES, J.Am.Chem.Soc., 94, 7074 (1972).
5. S. GALAJ and Y.L. PASCAL, Bull.Soc.Chim.Fr., 3979 (1972).
6. S. HOLLAND, R. EPSETEIN and I. MARSZAK, Bull.Soc.Chim.Fr., 3213 (1969).
7. E.J. COREY and A. VENKATESWARLU, J.Amer.Chem.Soc., 94, 6190 (1972).
8. The spectrum of 3 can be interpreted in a alternative manner also ; it is possible to interchange H_1 with H_2 and H_2 with H_3. However, the signal at 5.96 p.p.m. is the most sensitive to the effects of the solvents (CCl_4, benzene : $\Delta\delta$ = 0.44 p.p.m.). It is probably due to the proton situated between the two OTms groups i.e, H_4.
9. R.B. WOODWARD and R. HOFFMANN, Ang.Chem.Internat.Ed., 5, 385 (1967).
10. V. KLEVELAND and L. SKATTEBØL, Chem.Comm., 432 (1973).
11. W.D. HUNTSMAN and H.J. WRISTERS, J.Amer.Chem.Soc., 89, 342 (1967).
12. a) A. LIBERLES, A. GREENBERG and J.E. EILERS, J.Chem.Educ., 50, 676 (1973).
    b) N. EPIOTIS, J.Amer.Chem.Soc., 95, 3087 (1973).
    c) P. KOLLMAN, J.Amer.Chem.Soc., 96, 4363 (1974).
13. Cis 1-methyl-2-methoxy ethylene is more stable than the trans isomer by 0,53 Kcal.mole^{-1} (P. SALOMAA and P. NISSI, Act.Chem.Scand., 21, 1386 (1967)). Besides, the synthesis of 1-methyl-2-trimethylsiloxyethylene leads to a higher percentage of cis isomer under equilibrium conditions (H.O. HOUSE, L.J. CZUBA, M. GALL and H.D. OLMSTEAD, J.Org.Chem., 2324, (1969).