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MIGRATION APTITUDES OF UNSATURATED GROUPS IN THERMAL [1,5]-SIGMATROPIC REARRANGEMENTS

P. Schiess and P. Fünfschilling
Institut für Organische Chemie, Universität Basel, Switzerland

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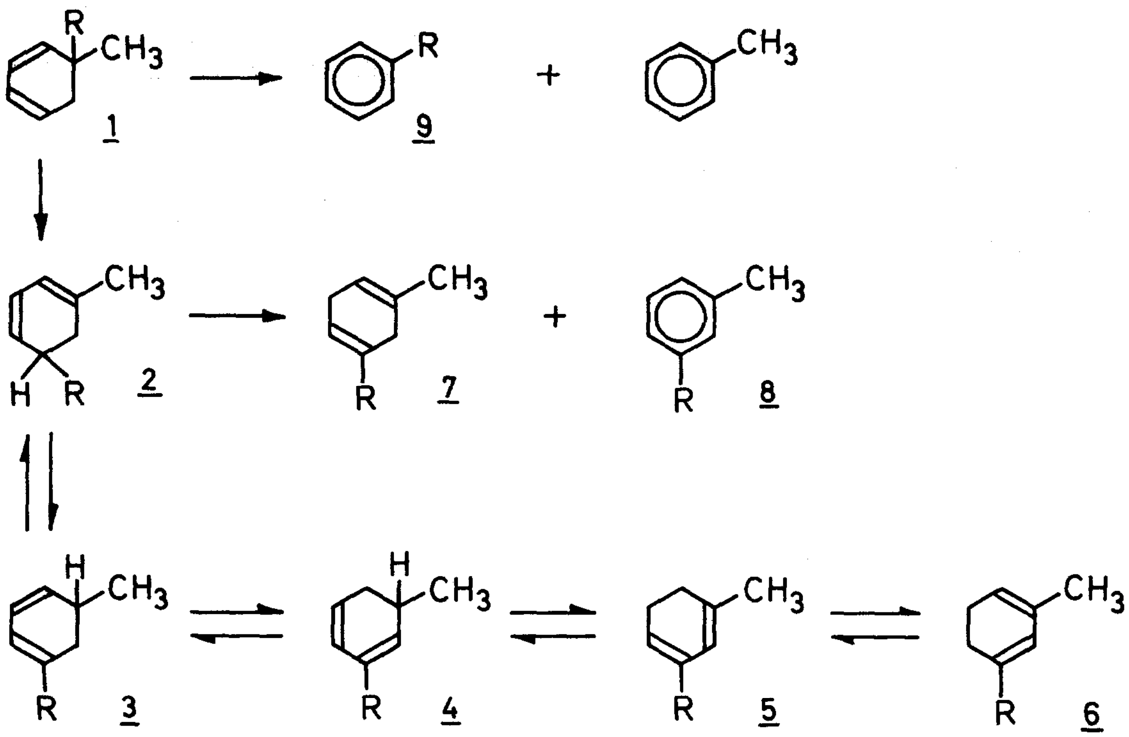
In the preceeding communication 1) we have shown that the aldehyde group in 1-formylcyclohexa-2,4-dienes competes with hydrogen in its tendency to undergo an uncatalyzed intramolecular [1,5]shift 2). We wish to report here the result of a study of the thermal reactions of 1-carbomethoxy-1-methyl-cyclohexa-2,4-diene (1a, R = $COOCH_3$) and of its 1-acetyl- and 1-formyl-analogue 1b (R = $COCH_3$) and 1c (R = CHO). These compounds were expected to react at elevated temperature through a [1,5]shift of the unsaturated group R. A comparison of their reactivity with that of 1-methylcyclohexa-2,4-diene (1d: R = H) for which the rate of [1,5]-hydrogen migration is known 3) should allow assignments to be made for migration aptitudes of different groups R relative to hydrogen in thermal [1,5]sigmatropic rearrangements.

Compounds 1b (bp. 70-72°/12 torr; UV.(C_2H_5OH): 258 nm (4040); IR.(film): 1707 cm^{-1}; NMR.(CCl_4): δ 1.15 s 3H, 2.08 s 3H, 1.9-2.9 m 2H, 5.6-6.0 m 4H; 2,4-dinitrophenylhydrazone: mp. 109-110°) and 1c (bp. 50-52°/12 torr; UV.(C_2H_5OH): 259 nm (3950); IR.(film): 2710, 1723 cm^{-1}; NMR.(CCl_4): δ 1.11 s 3H, 2,0-2,8 m 2H, 5.4-6.2 m 4H, 9.41 s 1H; 2,4-dinitrophenylhydrazone: mp. 122-123°) were obtained from 1-acetyl-1-methyl- and 1-formyl-1-methylcyclohex-3-ene respectively through bromination-dehydrobromination following the procedure for the preparation of 1a 4).

Vapour phase pyrolysis of methyl ester 1a leads to five of the six possible dihydro-meta-toluic esters having two conjugated, endocyclic double bonds (2a - 6a, see table I). A mixture of the same composition 2a - 6a is obtained upon pyrolysis of ester 4a 5). This indicates that equilibrium is reached between isomers 2a - 6a through multiple [1,5]H-shifts which occur faster than the primary rearrangement 1a $\longrightarrow$ 2a. The thermal stability of non conjugated ester 2a which participates in the reaction mixture with 16 % contrasts with the lability of ketone 2b and aldehyde 2c mentioned below. This stability of 2a reflects the lower tendency of β,γ-double bonds to shift into conjugation with an ester than with an aldehyde or ketone function.



a. $R = COOCH_3$ b. $R = COCH_3$
c. $R = CHO$ d. $R = H$

Gas phase thermolysis of 1c at 340° gives essentially the same products as are obtained from 1-methyl-[3,2,0]bicyclohept-2-en-7-one 1). This constitutes additional evidence for the formation of 1c as an unstable intermediate in the pyrolysis of the latter ketone 1). The large amount of 2,5-dihydro-meta-tolualdehyde 7c, assumed to be formed through an enolization-reprotonation process from 2c, is evidence for the high tendency of 2c to have its β,γ-double bond shift into conjugation with the carbonyl group. Apparently for dihydrotolualdehyde 2c, the primary rearrangement product of 1c, enolization (→ 7c) and aromatization (→ 8c) do compete effectively with [1,5]hydrogen migration, for conjugated aldehydes 3c - 6c are only minor reaction products of 1c.

Ketone 1b shows behaviour intermediate between that of 1a and 1c : In the gas phase more aromatization occurs than upon pyrolysis of the ester 1a and less of the 2,5-dihydro-isomer of structure 7 is formed than from aldehyde 1c. A minor product which did rearrange upon attempted separation by vpc is tentatively assigned structure 2b, the primary product expected from 1b.

Table I Products from pyrolysis of 1-methyl-cyclo-2,4-hexadienes 1 a) b)

		1	2	3	4	5	6	7	8	9	others c)
1a	506°/1 s d)	6	16	11	5	19	23	-	9	5	6
R = $COOCH_3$	288°/8 h e)	8	10	2	1	4	5	6 f)	48	2	14
1b	448°/1 s d)	3	4 f)	29	6 f)	1 f)	13	7 f)	23	1	13
R = $COCH_3$	200°/22 h e)	9	-	5	-	-	-	33 f)	45	-	8
1c	340°/1 s d)	5	-	9	-	-	4 f)	56	20	-	6
R = CHO	188°/1 h e)	12	-	-	-	-	-	20	63	-	5

a) All compounds in this table have been identified, except where indicated, by comparison with samples prepared independently or by IR-, UV- and NMR-spectra and by aromatization with chloranil. - b) Percentage of recovered pyrolysis product is given as determined by capillary vpc (recovery 80 - 90%). - c) Toluene and compounds of undetermined structure. - d) Vapour phase pyrolysis in a flow system, 11 torr. - e) Reaction in heptane solution. - f) Tentative structural assignment.

A small amount of non methylated aromatic products 9 obtained from 1a and 1b but not from 1c indicates that in the former compounds cleavage of the $C-CH_3$ bond competes to a minor extent with migration of the unsaturated group R. Aromatization of the crude pyrolysis mixtures from 1a, 1b and 1c with chloranil did produce meta-substituted aromatic products 8 exclusively 6) demonstrating the high regiospecificity of the rearrangement process.

Aldehyde 1c and, to a lesser extent, ketone 1b and ester 1a are slowly converted into toluene even at room temperature in the absence of radical inhibitors. Pyrolysis in solution therefore had to be carried out in the presence of hydroquinone in order to prevent extensive radical induced decomposition. Under these conditions aromatization prevails and less of the meta-dihydroproducts 2 - 7 are formed than in the gas phase experiments. Rate measurements conducted in n-heptane solution yield first order rate constants for the disappearance of 1a, 1b and 1c from which activation parameters were calculated (table II).

Rearrangement of aldehyde 1c has been shown to proceed through a [1,5]formyl-migration 1). Similar Arrhenius factors for the rearrangement of 1a and 1b as for 1c indicate that all three compounds of structure 1 do react by the same primary step. The question raised recently 2a) whether a [1,5]shift of an unsaturated group proceeds in a single step or actually involves a sequence of two consecutive [1,3]-shifts can be answered for the carbomethoxy group: 1-carbomethoxy-3-methyl-2,5-cyclohexadiene 7), the product expected from 1a through a single [1,3]shift of the ester group, does yield meta-toluic ester 8a almost exclusively upon gasphase pyrolysis at 500°; it therefore cannot be an intermediate in the rearrangement of 1a.

Table II Kinetic data for rearrangement of cyclohexadienes 1.

	Temp. range	$k_1 \cdot 10^4$ (230°, s^{-1})	E_a (kcal/mol)	log A (sec^{-1})
1a, R = $COOCH_3$ a)	270-304°	0.014	40.8 ± 1.8 c)	11.8 ± 0.7 c)
1b, R = $COCH_3$ a)	200-240°	3.98	35.9 ± 1.0	12.1 ± 0.4
1c, R = CHO a)	150-200°	125	31.0 ± 0.6	11.5 ± 0.3
1d, R = H b)	300-360°	1.00	35.2	11.2

a) heptane solution b) gas phase [3] c) 95 % confidence limit

From our rate measurements (table II) it can be seen that in the 1-methylcyclohexa-2,4-diene system (1) formyl gives [1,5]sigmatropic shifts faster than hydrogen by more than two orders of magnitude whereas the carbomethoxy- group is slower by a factor of about 70, acetyl showing comparable migration aptitude as hydrogen. Possible explanations for the wide difference in reactivity of these unsaturated groups towards sigmatropic rearrangement are actively tested in our laboratory.

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FOOTNOTES

1) P. Schiess and P. Fünfschilling, preceeding communication.

2) There are several recent reports of thermal [1,5]shifts of unsaturated groups: Carbomethoxy-migration: a) J.A. Berson and R.G. Solomon, J. Amer. Chem. Soc. 93, 4621 (1971); b) R.A. Baylouny, ibid. 93, 4621 (1971); c) D.E. McGreer and Y.Y. Wigfield, Can. J. Chem. 47, 2095 (1969); d) P. Schmidt, R.W. Hoffmann and J. Backes, Angew. Chem. 84, 534 (1972). - Ketimine-migration: e) G. Maier, I. Fuss and M. Schneider, Tetrahedron Letters 1970, 1057; f) M. Mahendran and A.W. Johnson, Chem. Comm. 1970, 10. Amid-migration: g) D.W. Jones and G. Keen, Chem. Comm. 1971, 1356. - Phenyl-migration: h) L.L. Miller and R.F. Boyer, J. Amer. Chem. Soc. 93, 650 (1971); i) D. Beck and K. Schenker, Helv. 54, 734 (1971).

3) P. Van der Burg, Dissertation, Leiden 1970; we wish to thank Professor Havinga for having made available to us a copy of this thesis.

4) J. Wolinski, R. Novak and R. Vasileff, J. Org. Chem. 29, 3596 (1964).

5) G.A. Berchtold, J. Ciabattoni and A.A. Tunick, J. Org. Chem. 30, 3679 (1965).

6) Detection limit for ortho or para product: 0.5 %.

7) Prepared from the acid: O.L. Chapman and P. Fitton, J. Amer. Chem. Soc. 85, 41 (1963).