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SYNTHESIS AND KINETIC STUDY ON THE RETRODIENE DECOMPOSITION OF NORBORNENE-CONDENSED 1,3-OXAZIN-4-ONES

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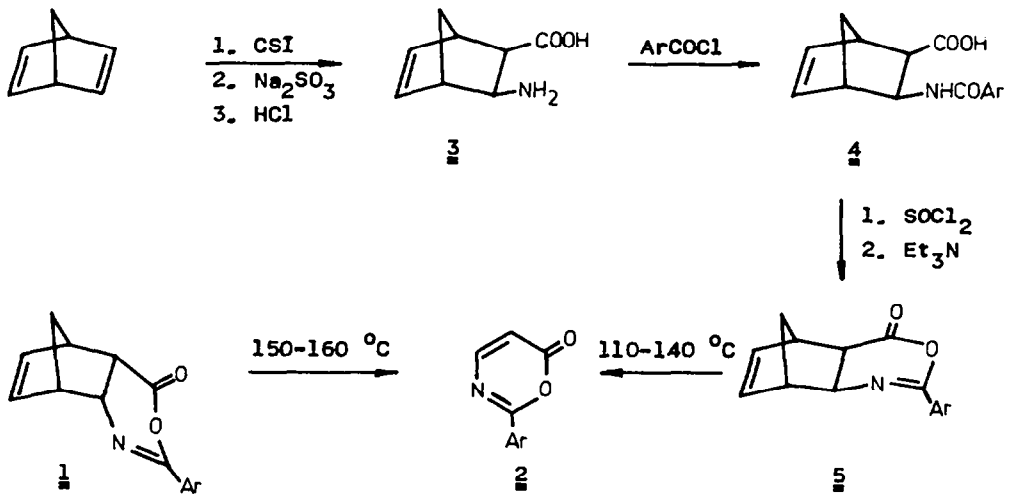
Abstract - The cis-exo-amino acid 3 with norbornene skeleton was converted into 2-aryl-cis-exo-1,3-oxazin-4-ones 5a-d. These compounds, similarly to the diendo isomers 1a-d studied by us earlier, undergo retrodiene decomposition under mild conditions to give 2-aryl-6H-1,3-oxazin-6-ones (2a-d) in 50-60% yield. The ratio of the decomposition rate constants of the tricyclic diendo and diexo-1,3-oxazin-4-ones, measured in toluene solution, is about 2.

In previous communications we reported the syntheses of tri-, tetra- and pentamethylenedihydro- and -tetrahydro-1,3-oxazines, as well as their 2- and 4-one and -thione derivatives[2-6], and also the spectroscopic investigation[7-9] of these compounds, our aim being comparative stereochemical and pharmacological studies. Since cis-trimethylene-condensed 1,3-oxazinones displayed considerable biological activity[10], the investigations were extended to compounds with an ethylene or ethenylene bridge in the cyclopentane ring, i.e. to derivatives with a condensed norbornane or norbornene skeleton[11-13]. The present work deals with the synthesis and the kinetics of the facile retrodiene decomposition of methylene-bridged tetrahydro-4H-3,1-benzoxazin-4-ones (5), and with the resulting 6H-1,3-oxazin-6-ones (2).

We recently briefly described the synthesis and thermolytic decomposition of the 2-aryl-5,8-methano-r-4a,t-5,t-8,c-8a-tetrahydro-4H-3,1-benzoxazin-4-ones (1a-d), leading to the 2-aryl-substituted derivatives 2[14]. As an alternative mode of preparation and for purposes of kinetic comparison, the retrodiene reaction was also applied to the isomeric compounds 5. The 3-exo-aminobicyclo-[2.2.1]hept-5-ene-2-exo-carboxylic acid (3) was prepared by cycloaddition of norbornadiene and chlorosulphonyl isocyanate according to the literature[15], except that addition was performed at 0 °C instead of -40 °C. The chlorosulphonyl derivative was reduced with sodium sulphite[16], and the resulting azetidinone transformed to the cis-exo-amino acid 3[15] (Scheme).

The amino acid 3 was cyclized to the 2-aryl-5,8-methano-r-4a,c-5,c-8,c-8a-tetrahydro-4H-3,1-benzoxazin-4-ones (5) by preparing the amides 4; these were



3 **4** **1** **2** **5**

a: Ar = C_6H_5; **b**: Ar = $C_6H_4CH_3$(p); **c**: Ar = C_6H_4Cl(p); **d**: Ar = $C_6H_3Cl_2$(m,p)

Scheme

treated with thionyl chloride, followed by triethylamine. The new 1,3-oxazin-4-ones have melting points lower by about 20 °C than those of the cis-endo isomers **1**, and their pyrolytic decomposition occurs on melting. The resulting **2a-d** 1,3-oxazin-6-ones can be isolated in 50-60% yield, which is similar to that obtained on starting from the isomers **1**. Thus, the present milder conditions of pyrolysis offer no preparative advantage.

Kinetic measurements were also carried out to compare the thermolytic decompositions of the tricyclic cis-endo- **1a-d** and cis-exo-1,3-oxazines **5a-d**. Quantitative determination of the decomposition products **2** was based on the characteristically different UV absorption of the starting materials **1** or **5** and the products **2**. Compounds **1** and **5** have absorption maxima at 245 nm in ethanol or n-hexane solution, whereas the absorption peak for the 1,3-oxazin-6-ones **2** is at 310 nm. The UV spectra of compounds **2** are the same in toluene or chlorobenzene solution. Use of these two solvents in kinetic measurements has advantages, partly because of the higher boiling points (chlorobenzene, 138.2 °C; toluene, 110.6 °C), and partly because the ethanolysis of compounds **1** and **5**, as well as that of **2** (reported for the related tetramethylene-1,3-oxazin-4-ones[17]), is thereby excluded. Our measurements were made in toluene ($\varepsilon_{20\ ^oC}$ = 2.29) and the more polar chlorobenzene ($\varepsilon_{20\ ^oC}$ = 10.3) in the temperature range 110-130 °C. The substituents on the 2-phenyl group had practically no effect on the UV maxima of compounds **1**, **2** and **5**.

The first-order decomposition rate constants of compounds **1** and **5** were calculated from the UV absorption changes of the 10^{-3} mol/litre solutions, the concentration of the product **2** being determined. Table 4 lists the rate constants and activation energies. The decomposition rate constants of the tricyclic diendo derivatives **1** in toluene at 120 °C are about twice as high as those of the diexo isomers **5**. The solvent and para substituents on the phenyl group have hardly any influence on the rate. No significant difference is seen in the calculated activation energies.

Table 1. Characteristic IR frequencies (cm^{-1}) and ^1H NMR chemical shifts (δ, ppm) for compounds 1a-d, 2a-d and 5a-d

Compound	H-5[a] H-4a[b]	H-4[a] H-8a[b]	H-5[c] (1H)	H-6 m (1H)	H-7 m (1H)	H-8[c] (1H)	H-9[d] (2H)		H-2',6' m (2H)	H-3',5' m (2H)	H-4' m (1H)	CH_3 s (3H)	ν C=O band	ν C=N band[i]
1a	3.12	4.46	3.47	6.21	6.17	3.55	1.45	1.56	7.93	7.4 m (3H)[e]		-	1750	1680
1b	3.10	4.45	3.48	6.20	6.12	3.55	1.45	1.55	7.82	7.18	-	2.36	1755	1685
1c	3.15	4.50	3.48	6.25	6.15	3.57	1.47	1.58	7.88	7.36	-	-	1760	1680
1d	3.16	4.48	3.49	6.23	6.12	3.58	1.49	1.59	8.40[f] 7.76[g]	7.46[h]	-	-	1763	1688
2a	6.22	7.82	-	-	-	-	-		8.22	7.50	7.60	-	1750	
2b	6.18	7.80	-	-	-	-	-		8.09	7.28	-	2.42	1730	
2c	6.22	7.81	-	-	-	-	-		8.14	7.46	-	-	1755	
2d	6.25	7.82	-	-	-	-	-		8.32[f] 8.05[g]	7.58[h]	-	-	1765	
5a	2.57	3.86	3.24	6.36	6.28	3.42	1.40	1.50	8.02	7.35-7.55 (3H)[e]		-	1760[i] -1770[i]	1695[i] -1700[i]
5b	2.55	3.80	3.22	6.35	6.30	3.40	1.38	1.50	7.91	7.22	-	2.39	1770	1685
5c	2.58	3.80	3.23	6.35	6.30	3.42	1.38	1.52	7.97	7.40	-	-	1762	1690
5d	2.59	3.86	3.24	6.35	6.30	3.42	1.35	1.52	8.12[f] 7.85[g]	7.49[h]	-	-	1760	1695

[a] d, 1H (A or B part of an AB spectrum), $J_{AB} \approx 6.8$ Hz

[b] dd, 1H, $J(4a,8a) \approx 8$ Hz, $J(4a,5) \approx J(8,8a) \approx 4$ Hz (1a-d) or d, 1H, $J(4a,8a) \approx 8$ Hz, $J(4a,5) < 1$ Hz (5a-d)

[c] singlet-like broad signal

[d] AB spectrum $J_{AB} \approx 9$ Hz

[e] overlapping multiplets of H-3',5' and H-4'

[f] H-2

[g] H-6

[h] H-5

[i] split bands

[j] for 2a-d, bands of group frequencies of the delocalized π-system appear instead of a ν C=N band

Table 2. ^{13}C NMR data (δ, ppm) on compounds 1a–d, 2a–d and 5a–d

Compound	C-2	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-9	C-1'	C-2',6'	C-3',5'	C-4'	CH_3
1a	?	?	46.7[b]	45.5[b]	136.6[a]	135.7[a]	49.7[b]	60.3	41.3	?	127.8[c]	128.3[c]	131.4	-
1b	149.9	166.7	46.7[b]	49.4[b]	136.6[a]	135.3[a]	49.7[b]	60.2	41.2	?	129.0[c]	129.3[c]	141.9	21.4
1c	149.1	166.4	46.8[b]	49.5[b]	136.6[a]	135.5[a]	49.7[b]	60.4	41.3	?	129.1[c]	128.7[c]	138.0	-
1d	148.1	166.0	46.8[b]	49.5[b]	136.5[a]	135.5[a]	49.6[b]	60.4	41.3	135.9[c]	129.4[d] 127.2[e]	131.0[f] 128.8[g]	133.0[c]	-
2a	158.1	154.6	-	109.6	165.1	-	-	-	-	140.8	128.8[a]	128.9[a]	133.5	-
2b	158.3	154.7	-	109.1	165.2	-	-	-	-	140.6	129.7[a]	128.9[a]	144.5	21.7
2c	157.8	154.4	-	109.8	164.1	-	-	-	-	140.2[b]	130.0[a]	129.4[a]	140.5[b]	-
2d	157.3	154.2	-	110.2	154.2	-	-	-	-	138.2	131.0[d] 130.4[e]	129.8[f] 127.5[g]	133.7	-
5a	?	167.0	44.6	49.4[a]	138.5[b]	136.7[b]	51.5[a]	59.4	40.5	?	127.9[c]	128.4[c]	131.7	-
5b	150.3	167.0	44.5	49.3[a]	138.4[b]	136.6[b]	51.4[a]	59.2	40.4	?	127.8[c]	129.1[c]	142.1	21.4
5c	149.1	166.2	44.4	49.1[a]	138.3[b]	136.4[b]	51.2[a]	59.2	40.3	?	128.9[c]	128.5[c]	137.7	-
5d	148.5	166.3	44.6	49.4[a]	138.6[b]	136.6[b]	51.4[a]	59.6	40.5	136.2	130.5[d] 126.8[e]	130.8[f] 129.8[g]	133.1[c]	-

[abc] reversed assignment is also possible

[d] C-2'

[e] C-6'

[f] C-3'

[g] C-5'

The above retrodiene decomposition is a convenient procedure for the synthesis of 2-aryl-6H-1,3-oxazin-6-ones, which are difficult to obtain by other routes. Though several methods of synthesizing this group of compounds are known, e.g.[18-22], to our knowledge only a single 2-substituted derivative has been prepared, by gas-phase pyrolysis of methyl (2-phenyl-5-oxo-2-oxazolin-4-yl)acetate, involving ring expansion[23].

In contrast with other retrodiene reactions, which usually require much more drastic conditions, the pyrolysis occurs here at the melting points of the compounds (heated in an oil-bath): 150-160 °C for the endo isomers 1, and 110-140 °C for the exo compounds 5. The kinetic measurements showed that decomposition also takes place in toluene or chlorobenzene, at temperature considerably lower than the melting point. Only a few procedures have been reported[24-30] for the retrodiene preparation of other heterocycles under similarly mild conditions.

In previous retro Diels-Alder reactions the adduct, prepared in one step, already contained the desired heterocycle; another novel feature of the present process is that the diene is used as a carrier in the building-up of the required molecule in several steps, and pyrolytic decomposition is effected subsequently.

The facile decomposition of tricyclic 1,3-oxazin-4-ones is explained by the formation of a heteroaromatic compound, conjugated with the 2-aryl group, when cyclopentadiene (acting as a protective group during the synthesis) is eliminated.

The described method of synthesizing compounds 2 is applicable only to 2-aryl derivatives; attempted cyclization of aliphatic amides 4, prepared with acetyl chloride from the amino acid 3, failed to give the homogeneous compound 5.

IR, ^{1}H and ^{13}C NMR spectra

The IR, ^{1}H and ^{13}C NMR data on compounds 1a-d, 2a-d and 5a-d listed in Tables 1 and 2.

The endo-endo or exo-exo anellation of the oxazinone ring to the norbornene skeleton in compounds 1a-d and 5a-d, respectively, is proved by the double doublet or doublet splitting of the H-8a signal[12] in the ^{1}H NMR spectrum. The dihedral angle of the H-C_{8a} bonds is ~50° in the endo-endo isomers, and in ~90 ° in the exo-exo isomers. Consequently, in compounds 5a-d, due to the Karplus relation[31], no splitting is expected, for the H-8,H-8a vicinal spin-spin interaction and the H-4a,H-8a interaction give a doublet[12].

The assignments of the signals are based on interrelations between the series discussed in this paper and the 4-deoxy analogues described earlier[12], where double resonance and differential NOE were used to prove the assignments.

For 2a-d, of course, the proton and carbon signals of the norbornene moiety are absent, and the ^{1}H and ^{13}C spectra exhibit instead the AB multiplet of H-4,5 and the lines of C-4,5 in the oxazinone ring, respectively.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded at 250 MHz and 63 or 20 MHz, respectively, in $CDCl_3$ solution (δ_{TMS} = 0 ppm) with a Bruker WM-250-FT spectrometer; IR spectra were obtained on a Bruker IFS-113V-FT instrument.

3-exo-Aminobicyclo[2.2.1]hept-5-ene-2-exo-carboxylic acid 3

Norbornadiene (20.3 g; 0.22 mol) was dissolved in dry ether (100 ml) at 0 °C, and a solution of chlorosulphonyl isocyanate (31.1 g; 0.22 mol) in ether (40 ml) was added dropwise at the same temperature, with stirring. Stirring was continued until the mixture had warmed up to room temperature and a sample gave no vigorous reaction with water. The mixture was then cooled again to 0 °C and water (50 ml) was added by drops, with cooling and stirring. The ether phase was washed with water (2x50 ml) and dried (Na_2SO_4), and the ether was evaporated off. The residue was dissolved in benzene (40 ml) and added, dropwise and with stirring, to a mixture of Na_2SO_3 (22.0 g) in water (70 ml) and benzene (40 ml); during this procedure the aqueous phase was kept slightly alkaline by the addition of 10% KOH. The organic phase was separated and dried (Na_2SO_4), and the solvent was evaporated off. The solid residue was treated, under external cooling, with just enough conc. HCl to cover the product. In a few minutes a vigorous exothermic reaction ensued; when this was over, the product was dissolved in water (100 ml) and the mixture was evaporated to dryness. Addition of water (20 ml) and evaporation was repeated twice to eliminate all excess HCl. The residue was dissolved in water (200 ml) and transferred to a Dowex 50 ion-exchange resin column in acid form. The column was washed with water until neutral, and the amino acid 3 was eluted with a 1:1 mixture (2000 ml) of conc. NH_4OH and water. The residue obtained after evaporation of the eluate was dissolved in water (50 ml), the solution was filtered, and acetone was added until turbidity appeared. Crystallization at +4 °C gave a white crystalline product (14.4 g, 42.7%), m.p. 256-258 °C. (Found: C, 62.56; H, 7.31; N, 9.02. $C_8H_{11}NO_2$ requires: C, 62.73; H, 7.24; N, 9.14 %).

N-Acyl-3-exo-aminobicyclo[2.2.1]hept-5-ene-2-exo-carboxylic acid 4a-d

3-exo-Aminobicyclo[2.2.1]hept-5-ene-2-exo-carboxylic acid (3) (3.0 g; 0.22 mol) was dissolved in 10% NaOH (40 ml), the appropriate acid chloride (0.022 mol) was added, and the solution was stirred for 1 h. The solution was then acidified with HCl, and the precipitated product 4a-d was filtered off, washed with water, dried and crystallized from EtOH. The compounds prepared are listed in Table 3.

2-Aryl-5,8-methano-r-4a,c-5,c-8,c-8a-tetrahydro-4H-3,1-benzoxazin-4-ones 5a-d

The acyl derivative 4a-d (8 mmol) was allowed to stand with thionyl chloride (11.7 ml) for 30 min at room temperature. The excess of thionyl chloride was removed by evaporation to dryness below 30 °C. Ether was added and the evaporation was repeated twice. The residue was dissolved in benzene (20 ml), triethylamine (2.4 ml) was added, and the mixture was left to stand at ambient temperature for 20 h. The triethylamine hydrochloride precipitate was filtered off and the filtrate was evaporated. The residue was dissolved in dry benzene at room temperature and the same volume of dry ether was added. The colourless product was crystallized at 4 °C. The compounds prepared are listed in Table 3.

2-Aryl-6H-1,3-oxazin-6-ones 2a-d

The compound 5 (1.0 g) was heated in a dry flask at 150 °C for 10 min. The dark product was purified on a silica gel column, elution being performed with benzene. After evaporation of the solvent, the colourless crystalline products 2a[23] and 2h-d[14] were obtained.

Table 3. Physical and analytical data on the prepared compounds 4a-d, 5a-d

Compound	M.p., °C	Yield, %	Found, % C	H	N	Formula	Required % C	H	N
4a	200-202	90	70.14	5.65	5.63	$C_{15}H_{15}NO_3$	70.02	5.88	5.44
4b	199-201	92	70.72	6.24	5.25	$C_{16}H_{17}NO_3$	70.83	6.32	5.16
4c	206-208	90	61.50	4.62	4.65	$C_{15}H_{14}ClNO_3$	61.76	4.84	4.80
4d	201-203	89	55.42	4.17	4.42	$C_{15}H_{13}Cl_2NO_3$	55.24	4.02	4.29
5a	110-111	68	75.44	5.63	5.96	$C_{15}H_{13}NO_2$	75.30	5.48	5.85
5b	125-127	62	75.96	5.98	5.70	$C_{16}H_{15}NO_2$	75.87	5.97	5.53
5c	125-127	70	65.61	4.24	5.06	$C_{15}H_{12}ClNO_2$	65.82	4.42	5.12
5d	139-141	66	58.40	3.55	4.78	$C_{15}H_{11}Cl_2NO_2$	58.46	3.60	4.55

Kinetic measurements

The UV spectra were recorded with a Specord UV-VIS instrument; absorption was measured by means of a Spectromom 195 spectrophotometer with digital display. The concentration of 1, 2 and 5 was 10^{-3} mol/litre. For each series of measurement 8-10 ampoules of 2 ml capacity were used; these were flushed with nitrogen and charged with 2.00 ml of a solution in spectroscopically pure toluene or chlorobenzene. The sealed ampoules were placed in an ultrathermostat allowing temperature regulation with 0.1 °C accuracy. The ampoules were maintained at the required temperature (110, 115, 120, 125 or 130 °C) and after each 30-min period one of them was removed from the thermostat and cooled in ice-water; the solution was adjusted to 20±1 °C, 1 ml was diluted to 10.00 ml with toluene or chlorobenzene, and the absorption of the resulting solution was measured in a 1 cm quartz cell at 310 nm. Quantitative determination of compounds 2 was accomplished via a calibration plot.

Table 4. Rate constants and thermodynamic parameters of thermal decomposition of compounds 1 and 5

No	$k_1 \cdot 10^5$ sec^{-1} 383 K T[a]	383 K C[b]	388 K T	388 K C	393 K T	393 K C	398 K T	398 K C	403 K T	403 K C	$\Delta E^{\ddagger}$ kJ.mol^{-1} T	$\Delta E^{\ddagger}$ C	$\Delta S^{\ddagger}$ e.u. T	$\Delta S^{\ddagger}$ C
1a	2.36	2.95	3.96	4.99	6.51	8.21	10.60	13.40			126.9	127.7	-2.0	-2.0
5a			1.89	2.25	3.15	3.75	5.12	6.15	8.30	9.98	128.1	129.4	-3.8	-2.8
1b	2.41	2.96	4.15	4.92	6.62	8.05	10.80	13.40			126.4	129.4	-4.2	-2.8
5b			1.63	2.06	2.70	3.45	4.42	5.70	7.15	9.34	128.1	131.0	-4.0	-1.8
1c	2.81	3.15	4.62	5.23	7.52	8.62	12.20	14.10			123.9	126.0	-2.6	-2.9
5c			1.90	2.20	3.18	3.70	6.17	10.10	8.50	10.01	129.8	132.3	-2.8	-0.9
1d	2.81	3.22	4.76	5.38	7.95	9.04	13.20	15.10			129.8	129.8	-1.0	-0.7
5a			2.10	2.46	3.48	4.17	5.65	6.95	9.25	11.40	128.5	133.1	-3.5	-0.3

[a] T = toluene

[b] C = chlorobenzene

The first-order rate constants were calculated from the equation:

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

The activation energies were obtained with the empirical Arrhenius formula:

$$\Delta E^{\ddagger} = \frac{4.576 . T_1 . T_2 \log k_2/k_1}{T_2 - T_1}$$

where k_1 and k_2 are the rate conetants measured at the different temperatures.

The activation entropies were computed via the formula

$$\Delta S^{\ddagger} = 4.576 (\log k + \frac{\Delta H^{\ddagger}}{4.576\ T} - \log \frac{k}{h} T)$$

where $\Delta H^{\ddagger} = \Delta E^{\ddagger} - RT$. The results are shown in Table 4.

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