Acta Chemica Scandinavica B 31 (1977) 496—500

Intermolecular Hydride Transfer Reactions. VIII. Isomerisation of 2*H*- and 4*H*-Pyran Derivatives in Acetic Acid

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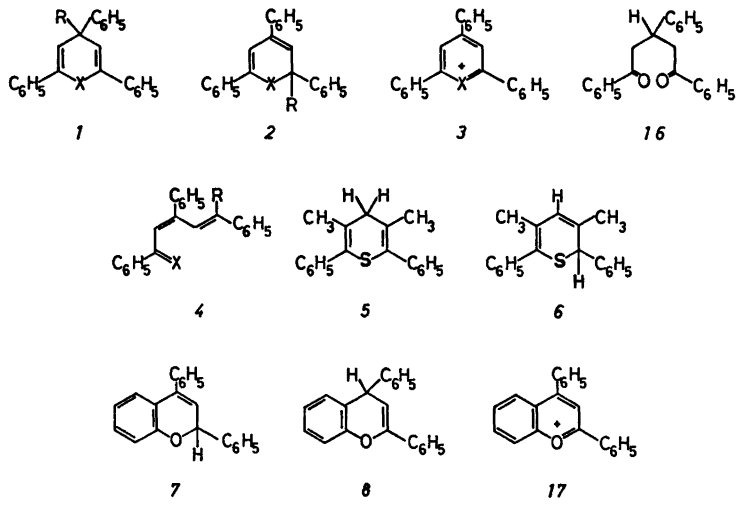
Isomerisation of 2*H*- and 4*H*-pyran derivatives in the presence of pyrylium cations has been studied. 2,4,6-Triphenyl-4*H*-thiopyran was quantitatively converted to the 2*H*-thiopyran in the presence of 2,4,6-triphenylthiopyrylium perchlorate in acetonitrile solution. The isomerisation was also obtained from treatment of the 4*H*-thiopyran with acetic acid. The 2,4,6-triphenylthiopyrylium cation was formed under the latter conditions. Isomerisation of 2,4,6-triphenyl-4*H*-pyran and 2,4-diphenylbenzo-2*H*-pyran to 1,3,5-triphenylpenta-2,4-dienone and 2,4-diphenylbenzo-4*H*-pyran, respectively, took place in boiling acetic acid. The mechanisms of these isomerisations are discussed.

Recently we reported [1] that interconversions of 2*H*- and 4*H*-pyran derivatives are catalysed by the corresponding pyrylium cation. Thus, 2,4,6-triphenyl-4*H*-pyran (*1a*, X = O) was isomerised to the 2*H*-pyran *2a* (X = O) in the presence of 2,4,6-triphenylpyrylium perchlorate (*3*, X = O) in acetonitrile solution. This isomerisation takes place through an intermolecular hydride transfer reaction (Scheme 1, and 2D). The 2*H*-pyran *2a* (X = O) is further con-



Scheme 1.

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verted to the open chain dienone structure *4* (X=O) through valence isomerisation. Earlier, the isomerisation of 3,5-dimethyl-2,6-diphenyl-4*H*-thiopyran (*5*) to the corresponding 2*H*-thiopyran *6* in acetic acid/HCl mixture was reported.[2] Intramolecular hydride transfer is suggested for this isomerisation (Scheme 1, and 2B). Oxidation of 2,4,6-triphenyl-4*H*-thiopyran (*1a*, X=S) to the pyrylium cation *3* (X=S) was observed in acetic acid/HCl solution.[2] However, formation of neither a pyrylium cation in addition to the isomerisation product nor an isomerisation product in addition to the oxidation product, was reported from reaction of *5* and *1a* (X=S), respectively, in acetic acid/HCl solution.

The purpose of the present work is to achieve isomerisation of 2*H*- and 4*H*-pyrans under the influence of acids with concurrent acid induced oxidation of the pyrans to pyrylium cations.

RESULTS

2,4,6-Triphenylthiopyrylium perchlorate (*3*, X=S) was quantitatively reduced with $NaBH_4$ to a 1:1 mixture of 2,4,6-triphenyl-4*H*-thiopyran (*1a*, X=S) and 2,4,6-triphenyl-2*H*-thiopyran (*2a*, X=S) in acetonitrile solution. Reduction with $NaBD_4$ afforded the γ-deuterated 4*H*-thiopyran *1b* (X=S) and the α-deuterated 2*H*-thiopyran *2b* (X=S).

The 4*H*-thiopyran *1a* (X=S) was isomerised to the 2*H*-thiopyran *2a* (X=S) in boiling acetic acid solution. Similar isomerisation of the γ-deuterated 4*H*-thiopyran *1b* (X=S) afforded exclusively the α-deuterated 2*H*-thiopyran *2b* (X=S).

A small amount of 2,4,6-triphenylthiopyrylium cation (*3*, X=S) was isolated as the perchlorate salt after prolonged boiling of *1a* (X=S) in acetic acid solution.

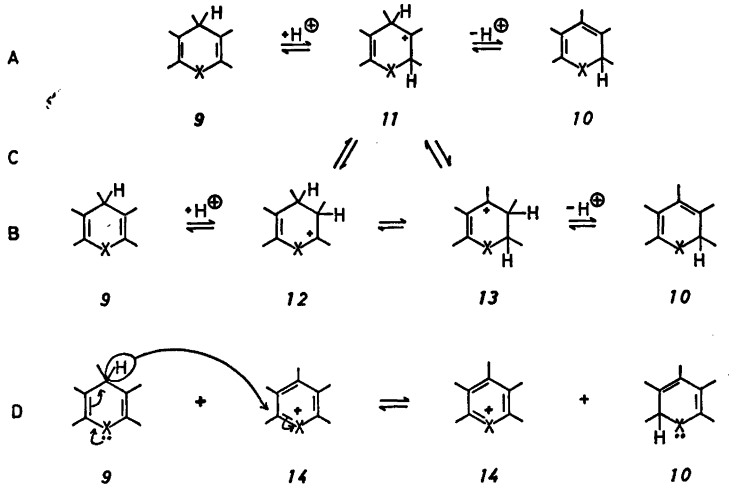
Isomerisation of the 4*H*-thiopyran *1a* (X=S) to the 2*H*-thiopyran *2a* (X=S) was not achieved in boiling acetonitrile solution. However, addition of the thiopyrylium perchlorate *3* (X=S) resulted in complete isomerisation. The thiopyrylium salt *3* (X=S) was recovered unchanged.

The rate of isomerisation of the 4*H*-thiopyran *1a* (X=S) in acetic acid solution was increased upon addition of the thiopyrylium salt *3* (X=S).

2,4,6-Triphenyl-4*H*-pyran *1a* (X=O) was isomerised to 1,3,5-triphenylpenta-2,4-dienone *4a* (X=O) in boiling acetic acid 1,3,5-Triphenylpenta-1,5-dione was observed as a by-product. 2,4-Diphenylbenzo-2*H*-pyran (*7*) was isomerised to 2,4-diphenylbenzo-4*H*-pyran (*8*) under similar conditions (Scheme 1).

DISCUSSION

Four mechanisms can be put forward to explain the isomerisation of 4*H*-pyrans *9* to 2*H*-pyrans *10* (and *vice versa*) (Scheme 2).



Scheme 2.

Acid catalysed isomerisation

A. Protonation at the α position of the 4*H*-pyran *9* with formation of the carbonium ion *11* which splits off the γ proton could give the 2*H*-pyran *10*.

B. Protonation at the β position of the 4*H*-pyran *9* with formation of the carbonium ion *12* and subsequent rearrangement (1,3 hydride shift) of *12* to the carbonium ion *13* which splits off the β proton could give *10*.

C. 1,2-Hydride shift in *11* to form *13* or two successive 1,2-hydride shifts in *12* to form *11* and *13* could give *10*.

Pyrylium cation catalysed isomerisation

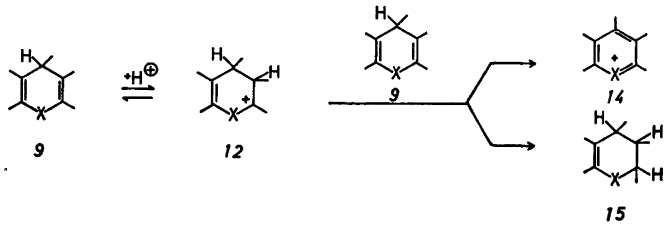
D. Intermolecular hydride transfer from the γ position of the 4*H*-pyran *9* to the α position of the pyrylium cation *14* could regenerate the pyrylium cation *14* and give the 2*H*-pyran 10.

Since the γ-deuterated 4*H*-thiopyran *1b* (X=S) afforded only the α-deuterated 2*H*-thiopyran *2b* (X=S) in boiling acetic acid, mechanisms A and C can be neglected. Deuterium/proton exchange with formation of the α-undeuterated 2*H*-pyran *2a* (X=S) in detectable amount (^{1}H NMR) would have been expected if these mechanisms were important. The isomerisation of the 4*H*-thiopyrans *1* (X=S) to the 2*H*-thiopyrans *2* (X=S) in acetonitrile solution in the presence of 2,4,6-triphenylthiopyrylium perchlorate (*3*, X=S) demonstrates that isomerisation is possible through mechanism D. Isolation of the thiopyrylium cation *3* (X=S) as the perchlorate salt (3 %) after prolonged boiling of the starting 4*H*-thiopyran *1a* (X=S) in acetic acid shows that the catalyst with respect to mechanism D, is formed under the condition of isomerisation.

Following the isomerisation of the 4*H*-thiopyran *1a* (X=S) in acetic acid (^{1}H NMR) it was observed that the rate was considerably increased after addition of a small quantity of the thiopyrylium perchlorate *3* (X=S).

A tentative explanation can be suggested to account for the formation of the pyrylium cation (*3*, X=S) from the 4*H*-thiopyran *1a* (X=S) in acetic acid solution (Scheme 3). Pyran derivatives *9* undergo acid induced disproportionation to give the corresponding pyrylium cations *14* and reduced pyran derivatives *15*.[3–5] The acids used for these purposes have been much stronger than acetic acid (HCl/CH_3COOH, $HClO_4/CH_3COOH$, CF_3COOH). Under such conditions the disproportionation is usually very fast and has resulted in isolation of pyrylium salts *14* in high yields. It seems likely that the rate of disproportionation is influenced by the equilibrium position of the protonation step (Scheme 3). The rate in weak acid may be slow due to a low concentration of the cation *12* which acts as a hydride acceptor in the redox step. The existence of an equilibrium between *9* and *12* was supported by ^{1}H NMR analysis of the products from treatment of the 4*H*-thiopyran *1a* (X=S) with deuterioacetic acid, which suggested a high degree of deuterium incorporation in the β positions. In acetic acid the disproportionation of *1a* (X=S) to *3* (X=S) seems to be slow, so slow that a concurrent isomerisation of *1a* (X=S) to *2a* (X=S) catalysed by *3* (X=S) can be observed.

Isomerisation of the 2,4,6-triphenyl-4*H*-pyran (*1a*, X=O) in boiling acetic acid solution resulted in isolation of the 1,3,5-triphenylpenta-2,4-dienone *4a* (X=O) (Scheme 1). In addition, the 1,3,5-triphenylpenta-1,5-dione (*16*) was observed as a byproduct. Formation of the latter compound can be explained from acid catalysed hydrolysis of the 4*H*-pyran *1a*



Scheme 3.

(X=O), due to the small concentration of water in the acetic acid.

Treatment of the 2,4-diphenylbenzo-2*H*-pyran (*7*) with acetic acid yielded the 2,4-diphenylbenzo-4*H*-pyran (*8*). The formation of *4a* (X=O) and *8* through isomerisation of *1a* (X=O) and *7*, respectively, is in agreement with the reported relative stabilities of the isomers.[1] It should be mentioned that the dienone *4a* (X=O) is supposed to be formed through valence isomerisation of the 2*H*-pyran *2a* (X=O). In this connection it is interesting to note that the dienone isomer *4a* is more stable than the 2*H*-pyran *2a* at 25 °C when X=O and that the relative stability seems to be reversed when X=S. Preliminary results (^{1}H NMR) from heating of the 2*H*-thiopyran *4a* (X=S) in neutral solution indicate ring cleavage above 90 °C.

EXPERIMENTAL

Reduction of 2,4,6-triphenylthiopyrylium perchlorate (*3*, X=S).

$NaBH_4$ (3.6 g, 0.096 mol) was gradually added (0.5 h) during stirring to a solution of 2,4,6-triphenylthiopyrylium perchlorate [6,7] (*3*, X=S) (10.0 g, 0.024 mol) in dry acetonitrile solution (300 ml). The reaction mixture was concentrated, added dry ether and filtered. The ethereal solution was extracted with water, dried and evaporated. The residual oil (7.5 g) was examined by ^{1}H NMR (see Table 1). Crystallisation from methanol gave pure 2,4,6-triphenyl-4*H*-thiopyran (*1a*, X=S). Yield 3.7 g (48 %): m.p. 110 °C:[8] ^{1}H NMR (60 MHz, $CDCl_3$):[9] δ 4.5 (1 H, *t*), 6.0 (2 H, *d*, *J* 4.0 Hz), 7.3 (15 H, *m*).

Similar reduction of *3* (X=S) with $NaBD_4$ gave 4-deuterio-2,4,6-triphenyl-4*H*-thiopyran (*1b*, X=S); m.p. 109 °C: ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.0 (2 H, *s*), 7.3 (15 H, *m*).

Isomerisation of 2*H*- and 4*H*-pyrans in acetonitrile solution.

The reported method [1] for isomerisation of pyran derivatives catalysed by pyrylium salts was used.

2,4,6-Triphenyl-4H-thiopyran (*1a*, X=S) was quantitatively isomerised to 2,4,6-triphenyl-2*H*-thiopyran (*2a*, X=S). The product was obtained as an oil and was identified by ^{1}H NMR.[9] ^{1}H NMR (60 MHz, $CDCl_3$: δ 4.97 (1 H, *d*), 6.0 (1 H, *d*, *J* 6 Hz), 6.93 (1 H, *s*), 7.3 (15 H, *m*).

Table 1. Preparation and isomerisation of 2*H*- and 4*H*-pyrans. Reaction period 12 h, reflux.

Hetero atom	Reactants (1:1)	Products	
Solvent CH_3CN			
S	*3*, $NaBH_4$ [a,b]	*1a*, *2a*	(1:1)
S	*3*, $NaBD_4$ [b]	*1b*, *2b*	(1:1)
S	*3*, *1a*	*3*, *2a*	(1:1)
S	*3*, *1b*	*3*, *2b*	(1:1)
S	*1a*	*1a* [d]	
O	*3*, *1a*	*3* *4a*	(1:1)
O	*17*, *7*	*17*, *8*	(1:1)
Solvent CH_3CO_2H			
S	*1a*	*2a*	
S	*1b*	*2b*	
S	*1a* [c]	*3* [d], *2a*	
S	*1a* [e]	*1a*, *2a*	(1:2)
S	*3*, *1a* [e,f]	*1a*, *2a*	(1:9)
O	*1a*	*16*, *2a*	(1:3)
O	*7* [g]	*8*	

[a] Excess. [b] 20 °C, 1 h. [c] 150 h. [d] 3 %. [e] 30 min. [f] 1:25. [g] 75 h.

4-Deuterio-2,4,6-triphenyl-4H-thiopyran (*1b*, X=S) yielded 2-deuterio-2,4,6-triphenyl-2*H*-thiopyran (*2b*, X=S). ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.0 (1 H, *s*), 6.93 (1 H, *s*), 7.3 (15 H, *m*).

Isomerisation of 2,4,6-triphenyl-4*H*-pyran (*1a*, X=O) and 2,4-diphenylbenzo-2*H*-pyran (*7*) by means of pyrylium catalysis has been reported earlier.[1] The results are included in Table 1.

Isomerisation of 2*H*- and 4*H*-pyrans in acetic acid solution.

2,4,6-Triphenyl-4*H*-thiopyran (*1a*, X=S) (0.96 g, 0.003 mol) in acetic acid solution (20 ml) was refluxed for 12 h. The solution was evaporated and the residue was examined by ^{1}H NMR. Only signals due to the 2*H*-thiopyran (*2b*, X=S) could be detected.

A similar solution of *1a* (X=S) was refluxed for 6 days. Addition of a hot saturated solution of $KClO_4$ in H_2O afforded a crystalline material after cooling. The precipitated material was collected, washed with hot water and recrystallised from acetic acid to yield 2,4,6-triphenylthiopyrylium perchlorate (*3*, X=S). Yield 3 %, m.p. 213 °C.

Two identical solutions of (*1a*, X=S) in acetic acid were prepared. To one of them was added the thiopyrylium perchlorate *3* (X=S) in molar ratio; *3*:*1a*=25:1. The solutions were refluxed for 0.5 h, evaporated and residues

were examined by ^{1}H NMR ($CDCl_3$). Results see Table 1.

*4-Deuterio-2,4,6-triphenyl-4*H*-thiopyran* (*1b*, X=S) (0.14 g) in [^{1}H]acetic acid solution (20 ml) was refluxed for 12 h. The solution was evaporated and the residue examined by ^{1}H NMR ($CDCl_3$) Only signals due to the 2-deuterio-2,4,6-triphenyl-2*H*-thiopyran (*2b*, X=S) were observed. No signals at δ 4.97 due to α protons could be detected.

*2,4,6-Triphenyl-4*H*-pyran* (*1a*, X=O)[1] (0.8 g, 0.0025 mol) in acetic acid solution (20 ml) was refluxed for 12 h. The solution was evaporated and the residue examined by ^{1}H NMR (CD_3COCD_3). Signals due to the 4*H*-pyran *1a* (X=O) could not be detected. All signals could be attributed to a mixture of 2,3,5-triphenylpenta-2,4-dienone *4a* (X=O)[1] and 1,3,5-triphenylpenta-1,5-dione (*16*). The former compound was isolated as a crystalline product on treatment of the residue obtained from the ^{1}H NMR sample with methanol. Yield 0.5 g, 62 %; m.p. 125 °C. Authentic 1,3,5-triphenylpenta-1,5-dione (*16*) (m.p. 85 °C)[10] was prepared for identification of this compound in the mixture mentioned above. ^{1}H NMR ($CDCl_3$): δ 3.31, 3.49, 4.07; AA'BB'X: J_{AB} −15 Hz, $J_{AX}=J_{BX}$ 7 Hz.

*2,4-Diphenylbenzo-2*H*-pyran* (*7*)[11] (0.9 g, 0.003 mol) in acetic acid solution was refluxed for 3 days. The solution was evaporated and the residue examined by ^{1}H NMR ($CDCl_3$). Only signals due to the 2,4-diphenylbenzo-4*H*-pyran (*8*)[12] could be detected. The 4*H*-pyran *8* was isolated as a crystalline product on treatment of the residue obtained from the ^{1}H NMR sample, with ethanol. Yield 0.72 g; 78 %; m.p. 109 °C.

Acknowledgement. A. A. Abdallah and M. M. Mishrikey are grateful for fellowships from the Norwegian Agency for International Development (NORAD).

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Received February 22, 1977.