Intermolecular Hydride Transfer Reactions. VI. Disproportionation Reactions of Flav-2-enes Induced by Acids

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The disproportionation reactions of flav-2-ene and closely related substances in different acids were studied. Through deuterium labelling experiments, the parent flav-2-ene was found to disproportionate faster than its 4-phenyl derivative. Fragmentation of 3-(flav-2-ene-4-yl)-2-methoxyflavane into flavylium cation and flav-2-ene was observed in perchloric and trifluoroacetic acid solutions. 4-Phenylflav-2-ene yielded the corresponding flavane on treatment with formic acid through a disproportionation sequence. Flavylium cations could be quantitatively reduced by means of formate anion. The possible mechanisms involved in these reactions are discussed.
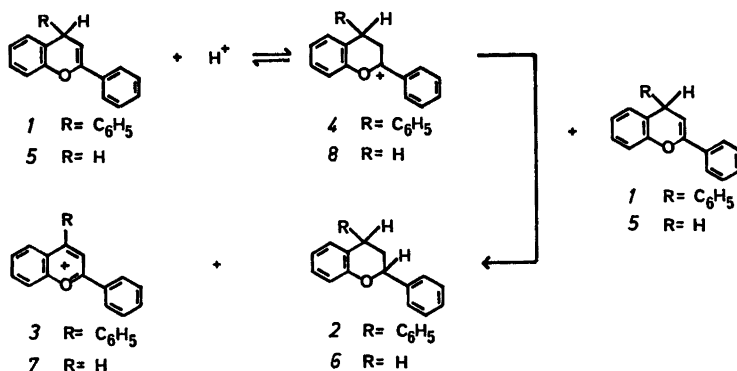
Recently we reported that the reaction of 4-phenylflav-2-ene (1) with trifluoroacetic (TFA) or perchloric acids afforded cis-4-phenylflavane (2) and the 4-phenylflavylium salt (3) in almost quantitative yields.[1] The mechanism of this

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acid-induced disproportionation reaction involves two steps (Scheme 1). The first is protonation of the 2-flavene (1) to yield the carbonium ion (4) which acts as a hydride acceptor in the second step.

In continuation of our studies of intermolecular hydride transfer reactions, the present work is devoted to investigation of the behaviour of some flavenes and closely related substances in different acidic media.

Boiling acetic acid was found to be incapable of effecting disproportionation of the 2-flavenes 1 and 5. The failure to observe the formation of the corresponding flavanes and flavylium acetates can be explained by supposing that the acid-induced reaction (Scheme 1) is thermodynamically unfavourable in this case due to the relatively weak acidity and strong nucleophilicity of acetic acid and its conjugate base, respectively. In an attempt to examine the reversibility of this reaction a mixture of

1 R= C₆H₅
5 R= H

4 R= C₆H₅
8 R= H

3 R= C₆H₅
7 R= H

2 R= C₆H₅
6 R= H

1 R= C₆H₅
5 R= H

Scheme 1.

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equimolar amounts of 4-phenylflavane (2), 4-phenylflavylium perchlorate (3) and potassium acetate in acetic acid solution was boiled for several hours. However, any formation of 4-phenylflavene (1), indicative of hydride transfer from the 4-phenylflavane (2) to the 4-phenylflavylium cation (3) followed by deprotonation of the resulting cation (4) by means of acetate anion, was not achieved. The disproportionation of flavenes requires protonation of the double bond with formation of a carbonium ion which can act as a hydride acceptor. Evidently, protonation of 1 takes place in boiling acetic acid since treatment of this compound with deuterioacetic acid afforded the 3-deuterio-4-phenylflav-2-ene (1, β-D). However, it seems likely that the exchange of the β-hydrogen of 1 can take place even though the equilibrium constant for protonation may be very small, too small to allow hydride acceptable to be important. On the other hand, this protonation-deprotonation sequence may not necessarily involve a carbonium ion sufficiently reactive to take part in a hydride transfer reaction. Thus, the failure of 1 to undergo disproportionation in acetic acid may be due to the lack of formation of a carbonium ion similar to the hydride acceptor 4 proposed to be formed in the stronger acid TFA.

The disproportionation reaction of 3-deuterio-4-phenylflav-2-ene (1, β-D) in deuteriotrifluoroacetic acid afforded cis-3,3-dideuterio-4-phenylflavane (2, β,β'-D) and 3-deuterio-4-phenylflavylium salt (3, β-D), the latter was isolated as the perchlorate. The deuterated products 2 (β,β'-D) and 3 (β-D) were also obtained from the disproportionation of the undeuterated 4-phenylflav-2-ene (1) in deuteriotrifluoroacetic acid. The ¹H NMR spectra of the products from the latter reaction revealed no signals due to the undeuterated analogues 2 and 3. Furthermore, only undeuterated products were obtained from the reaction of 1 (β-D) with TFA. These results indicate that in TFA, the exchange of the β-hydrogen of the 4-phenylflav-2-ene (1) occurs much faster than the disproportionation reaction.

The disproportionation of the parent flav-2-ene (5) into the flavane (6) and the flavylium cation (7) in 1:1 ratio was achieved with TFA as well as perchloric acid (Scheme 1). From the reaction carried out in deuteriotrifluoro-

acetic acid, a mixture of the flavylium salt (7) and its β-deuterio analogue (7, β-D) was isolated as the perchlorates. Based on the ¹H NMR spectrum of the salt mixture, the ratio between 7 and 7 (β-D) was estimated to be 1:1.

Assuming the hydrogen-deuterium exchange at the β-position of 1 and 5 to take place with comparable rates, the degree of deuterium incorporation in the flavylium salts offers a qualitative measure of the relative rates of the disproportionation reactions of the above flavenes in deuteriotrifluoroacetic acid solution. The formation of a mixture of the flavylium salts 7 and 7 (β-D) in a 1:1 ratio, and only the β-deuterated flavylium salt 3 (β-D) as mentioned above suggests that the γ-unsubstituted salt is formed much faster than the corresponding γ-phenyl substituted salt. It seems likely that the hydride acceptors 4 and 8 have comparable stabilities, since the positive charge at the α-position is stabilised by the same groups. With respect to the hydride donor ability, the creation of a positive charge at the γ-positions of 1 and 5 by removal of a hydride ion should be expected to occur easier with the former flavene (tertiary carbon) than with the latter (secondary carbon). From these considerations, the 4-phenylflav-2-ene (1) should be expected to undergo disproportionation faster than the parent flav-2-ene (5). However, since the opposite result was found through the deuterium labelling experiments, the rate controlling factors in these hydride transfer reactions seem to be related to steric effects exerted by the γ-substituent of 1 and 4, as well as the presence of two available hydrogens at the γ-position of the parent flav-2-ene (5).

Treatment of 2-methoxy-4-phenylflavane (9) with perchloric acid or TFA resulted in the formation of the flavylium cation (3) and cis-4-phenylflavane (2). This reaction presumably occurs through the intermediacy of 4-phenylflav-2-ene (1) formed by acid catalysed elimination of methanol from the ketal 9 (Scheme 2A), which subsequently disproportionates according to Scheme 1. The relative yields of the products support this conclusion.

Previously, it has been reported that hydride transfer to flavylium perchlorate (7) in methanol affords 3-(flav-2-ene-4-yl)2-methoxyflavane (10).[2,3] In the present work, the reaction
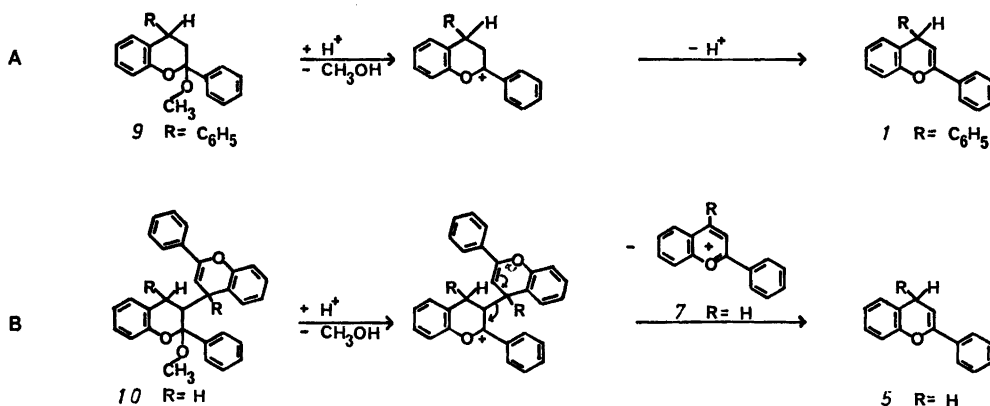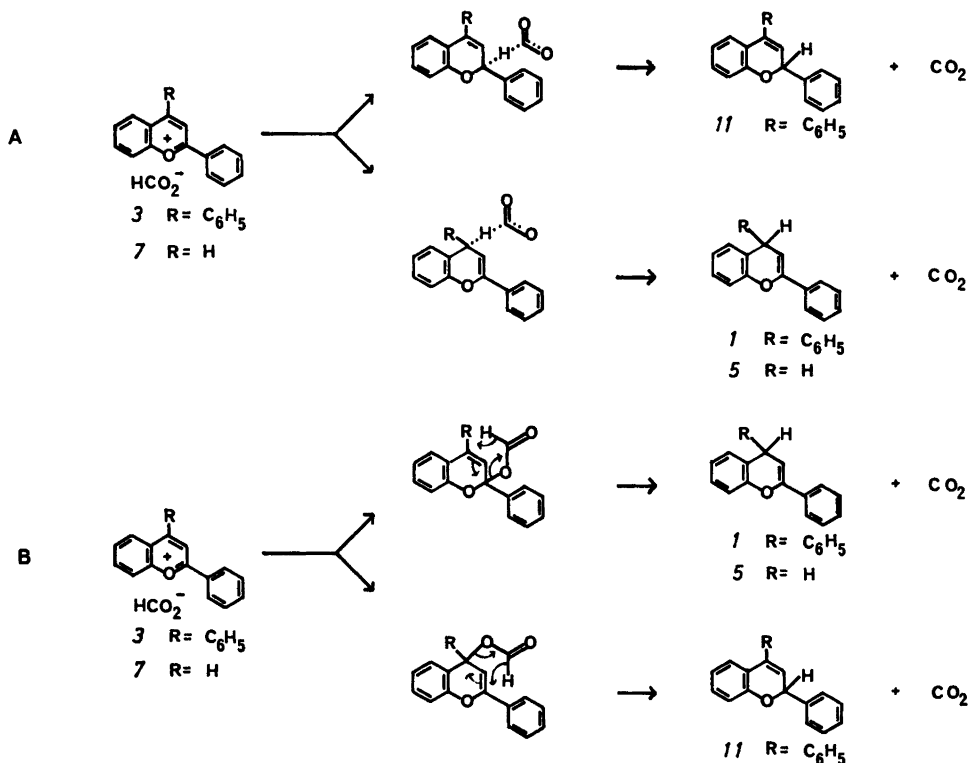
Scheme 2.

of the ketal *10* with TFA as well as perchloric acid was studied (Scheme 2B). The ¹H NMR spectrum of *10* in TFA showed signals due to the flavylium cation *7* and the flavane *6* in approximately 3:1 ratio. The flavylium salt was isolated as the perchlorate, while the formation of the flavane *6* was further verified by GLC. A similar result was observed with perchloric acid. The product distribution can be attributed to the fragmentation of the ketal *10* into the flavylium cation *7* and the flav-2-ene (*5*), which subsequently disproportionates according to Scheme 1. The fission of the carbon-carbon bond is the reverse of the sequence originally proposed by Reynolds and Van Allan [2] to account for the formation of *10* from flavylium perchlorate (*7*) and flav-2-ene (*5*) in methanol. It should be pointed out that similar fragmentation reactions have been reported to take place in the xanthene,[4] flavene,[5] and pyran [6] series.

Lempert-Sréter [7] has reported the formation of isobenzopyrylium formates from 2-(1-acetyl-propyl)benzophenones on treatment with formic acid and the subsequent transformation of these formate salts into the corresponding iso-benzochromenes. In the present work similar reduction of the flavylium cations *3* and *7* was achieved by means of formate anion. Treatment of the 4-phenyl-flavylium perchlorate (*3*) with sodium formate in boiling acetonitrile led to almost quantitative reduction of the former cation. The ¹H NMR spectrum of the ether soluble products revealed a 1:1 mixture of the 4-phenyl-flav-2-ene (*1*) and the corresponding 3-flavene

(*11*). The cation of the flavylium perchlorate (*7*) was also quantitatively reduced on similar treatment; however, the reaction resulted in the formation of the flav-2-ene (*5*) only (Scheme 3). The above results made it interesting to investigate the behaviour of the flavenes (*1* and *5*) in formic acid solution.

Considering formic acid to be sufficiently strong to induce disproportionation of the flavenes, the flavanes and flavylium formates should be initially formed in a 1:1 ratio. However, subsequent decomposition of the flavylium formates into flavenes susceptible to further disproportionation-decomposition sequences would remove the oxidation products formed through the disproportionation reaction. Alternatively, formation of only flavanes may be the outcome of a direct reduction of the vinyl ether group by means of formic acid. The latter reduction path seems to be generally accepted to account for the reduction reactions of the enamine group of dihydropyridines and quinolines by means of formic acid.[8–10]

Treatment of 4-phenylflav-2-ene (*1*) with boiling formic acid led to the separation of *cis*-4-phenylflavane (*2*) in 45 % yield on cooling. The ¹H NMR spectrum of the residual oil, obtained after evaporation of excess formic acid, exhibited signals due to the 4-phenyl-flavylium cation *3*. Moreover, subsequent addition of a perchloric-acetic acid mixture led to the isolation of the 4-phenylflavylium perchlorate (*3*) in 35 % yield. These yields of *2* and *3* indicate that the formation of the flavane (*2*) takes place mainly through a disproportio-

Scheme 3.

nation sequence rather than by a direct reduction of the vinyl ether group of the flavene by means of formic acid. Furthermore, the high yield of the flavylium salt was unexpected since decomposition of flavylium formate readily took place in acetonitrile solution as mentioned above. Hence, the above experiment was repeated and after isolation of the flavane 2 and removal of excess formic acid, the residual oil, mainly consisting of 4-phenylflavylium formate (3) was refluxed in acetonitrile. This treatment led to the formation of a mixture of 4-phenylflav-2-ene (1) and the corresponding 3-flavene (11) in a ratio of approximately 1:1. The total yield of these flavenes is comparable to the yield of cis-4-phenylflavane (2) isolated from the formic acid solution and hence correlates well with a quantitative decomposition of the 4-phenylflavylium formate (3), initially formed through a disproportionation reaction of the starting material in the formic acid solution. Thus, the ease of decomposition

of 4-phenylflavylium formate seems to be strongly dependent on the solvent used.

Treatment of the parent flav-2-ene (5) with boiling formic acid led to the formation of the flavane (6) in 80 % yield. No signals due to the flavylium cation 7 could be detected in the ^{1}H NMR spectrum of the residual oil after concentration of the reaction mixture. Assuming that the flavane (6) was formed through disproportionation-decomposition sequences, the high yield suggests that flavylium formate (7) undergoes decomposition much easier than the 4-phenyl substituted derivative 3 in formic acid. This may partly be attributed to the relative stabilities of these cations. The quantitative formation of 4-phenylflavylium perchlorate (3) and flav-2-ene (5) from an equimolar mixture of 4-phenylflav-2-ene (1) and flavylium perchlorate (7) shows that the former cation is more stable than the latter.

The decomposition of the flavylium formate salts discussed above can be considered to

take place through a neutral transition state by approach of the aldehydic hydrogen of the formate to the α or γ positions of the flavylium cation, followed by hydride transfer and carbon dioxide formation as shown in Scheme 3A. Alternatively, formate esters may be formed which subsequently rearrange to the flavenes with simultaneous evolution of carbon dioxide as represented in Scheme 3B. Similar mechanisms have been discussed by Stewart [11] to account for the formate reduction of the trityl cation. Stewart gave preference to the former route; however, the results from his kinetic and isotopic studies could not exclude any of these alternatives. In the present study, the reduction of the flavylium cations has not been followed kinetically. However, it should be pointed out that the rearrangement of the formate ester formed from the trityl cation requires a four-center transition state to yield triphenylmethane, while the formation of the flavenes may take place through a four-center, as well as a six-center transition state as indicated in Scheme 3B. The facile decomposition of the 4-phenylflavylium formate (3) in acetonitrile solution, may be attributed to the general decrease in solvation energy of anions in aprotic solvents.[12,13] A change of solvent from formic acid to acetonitrile should increase the nucleophilicity of the formate anion and hence increase the tendency towards formate ester formation. However, it seems reasonable that the hydride donor capacity (the reduction potential) of the free formate anion would increase through the same effect and consequently favour the decomposition path given in Scheme 3A. At the present stage in our investigation neither the observed solvent effects nor the product distribution seem to be conclusive with respect to the mechanism of the decomposition of the flavylium formates.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian A-60-A instrument with TMS as internal standard. A Perkin Elmer F11 instrument equipped with an OV-17 column was used for GLC analysis. The yields mentioned below were calculated according to the stoichiometry of the reactions. The compounds which were synthesized for the use as starting materials or for identification of products are listed below with their most characteristic ^{1}H NMR signals.

Flavylium perchlorate (7),[14] m.p. 180 °C. ^{1}H NMR in TFA: δ 8.70 (d, H_β), 9.47 (d, H_γ), $J_{\beta,\gamma} = 9.0$ Hz.

4-Phenylflavylium perchlorate (3),[1,15] m.p. 222 °C, ^{1}H NMR in TFA: δ 8.58 (s, H_β).

Flav-2-ene (5),[16] m.p. 54−55 °C. ^{1}H NMR in CDCl$_3$: δ 3.60 (d, 2 H_γ), 5.52 (t, H_β), $J_{\beta,\gamma} = 4.0$ Hz.

4-Phenylflav-2-ene (1),[17] m.p. 109 °C, ^{1}H NMR in CDCl$_3$: δ 4.85 (d, H_γ), 5.60 (d, H_β), $J_{\beta,\gamma} = 4.0$ Hz.

4-Phenylflav-3-ene (11),[17] m.p. 107 °C, ^{1}H NMR in CDCl$_3$: δ 5.82 (d, H_α), 5.90 (d, H_β). $J_{\alpha,\beta} = 4.0$ Hz.

Flavane (6), m.p. 43 °C, ^{1}H NMR in CDCl$_3$: δ 2.02 (m, H_β,H_β'), 2.87 (m, H_γ, H_γ'), 5.08 (4 lines, H_α), $|J_{\alpha,\beta} + J_{\alpha,\beta'}| = 12.0$ Hz.

cis-4-Phenylflavane (2)[1], m.p. 144 °C, ^{1}H NMR in CDCl$_3$: δ 2.30 (m, H_β, H_β'), 4.33 (4 lines, H_γ), $|J_{\beta,\gamma} + J_{\beta',\gamma}| = 17.6$ Hz, 5.19 (4 lines, H_α), $|J_{\alpha,\beta} + J_{\alpha,\beta'}| = 12.4$ Hz.

Reaction of the 2-flavenes (1) *and* (5) *with acetic acid*. 4-Phenylflav-2-ene (1) was recovered unchanged after refluxing its solution in glacial acetic acid for 72 h. cis-4-Phenylflavane (2) could not be detected by GLC analysis of the solution. Similarly no flavane (6) was detected in the solution of flav-2-ene (5) and glacial acetic acid after refluxing for 5 h.

3-Deuterio-4-phenylflav-2-ene (1, β-D). A solution of 4-phenylflav-2-ene (1) (1 g) in deuterioacetic acid (8 ml) was refluxed for 5 h. On cooling, 1 (β-D), crystallised out, m.p. 109 °C (ethanol 0.95 g, 95 % yield), ^{1}H NMR in CDCl$_3$: δ 4.85 (s, H_γ) and 6.9−7.8 (m, 14 aromatic H).

Treatment of 4-phenylflavylium perchlorate (3) *and potassium acetate with cis-4-phenylflavane* (2). A mixture of 4-phenylflavylium perchlorate (3) (0.19 g, 0.0005 mol), cis-4-phenylflavane (2) (0.15 g, 0.0005 mol) and anhydrous potassium acetate (0.05 g, 0.0005 mol) in glacial acetic acid (10 ml) was refluxed for 72 h. 4-Phenylflav-2-ene (1) could not be detected by GLC analysis of the solution.

cis-3,3-Dideuterio-4-phenylflavane (2, β,β'-D). A solution of 3-deuterio-4-phenylflav-2-ene (1, β-D) (0.3 g, 0.001 mol) in deuteriotrifluoracetic acid (TFA-d) (4 ml) was stirred at 20 °C overnight. The precipitated 2 (β,β'-D) m.p. 143−144 °C (0.14 g, 93 % yield) was collected by filtration. ^{1}H NMR spectrum in CDCl$_3$: δ 4.33 (s, H_γ), 5.20 (s, H_α) and 6.7−7.5 (m, 14 aromatic H).

3-Deuterio-4-phenylflavylium perchlorate (3, β−D). The filtrate from the above experiment was evaporated and the residue was treated with a mixture of 70 % perchloric acid and glacial acetic acid (1:10, 8 ml) followed by ether (100 ml) and kept overnight. 3-Deuterio-4-phenylflavylium perchlorate, (3, β-D) m.p. 222 °C (0.17 g, 85 % yield) which separated,

was collected by filtration. ¹H NMR spectrum in TFA: δ 7.8 – 8.4 (m, aromatic H).

Reaction of 4-phenylflav-2-ene (1) with TFA-d. The reaction of *1* with TFA-*d* carried out as described above afforded *cis*-3,3-dideuterio-4-phenylflavane (*2*, β,β'-D) in 70 % yield and 3-deuterio-4-phenylflavylium perchlorate (*3*, β-D) in 82 % yield.

Reaction of 3-deuterio-4-phenylflav-2-ene (1, β – D) with TFA. The reaction of *1* (β-D) with TFA carried out as described above afforded *cis*-4-phenylflavane (*2*), m.p. 144 °C (ethanol) in 66 % yield, and 4-phenylflavylium perchlorate (*3*) m.p. 222 °C in 70 % yield.

Disproportionation of: (a) *Flav-2-ene (5) in perchloric acid:* A solution of flav-2-ene (0.5 g, 0.0024 mol) in a mixture of 70 % perchloric and glacial acetic acids (1:10, 10 ml) was stirred at 20 °C overnight. Ether (100 ml) was added and the precipitated flavylium perchlorate (*7*) m.p. 178 – 180 °C, (0.25 g, 75 % yield) was filtered. Flavane (*6*) (0.19 g, 75 % yield) was obtained as an oil from the filtrate after washing with 10 % NaHCO₃, drying (MgSO₄) and evaporation and was identified by ¹H NMR.

(b) *Flav-2-ene (5) in TFA.* A solution of flav-2-ene (*5*) (0.50 g, 0.0024 mol), in TFA (8 ml) was stirred at 20 °C overnight. The ¹H NMR spectrum of this solution revealed the presence of the flavylium cation (*7*) and flavane (*6*) in approximately 1:1 ratio. The solution was evaporated and the residue was dissolved in a mixture of 70 % perchloric and acetic acids (1:10, 10 ml) followed by the addition of ether (100 ml). Flavylium perchlorate (*7*) m.p. 180 °C, (0.30 g, 80 % yield) which separated was filtered off. Flavane (*6*) (0.18 g, 72 % yield) was obtained from the filtrate after washing with 10 % NaHCO₃, drying (MgSO₄) and evaporation.

(c) *Flav-2-ene (5) in TFA-d.* The reaction of flav-2-ene (*5*) (0.30 g, 0.0014 mol) with TFA-*d* (3 ml) followed by treatment with a mixture of 70 % perchloric and acetic acids (1:10, 8 ml) as mentioned above led to the separation of a mixture of flavylium perchlorate (*7*) and 3-deuterioflavylium perchlorate (*7*, β-D) in 1:1 ratio (0.20 g, 90 % yield) m.p. 180 °C. The ¹H NMR spectrum of the mixture in TFA exhibited a singlet at δ 9.5 in between the H$_\gamma$ doublet of *7*. The rest of the spectrum was identical to that of *7* except for a decrease in the intensity of the H$_\beta$ doublet compared to the aromatic proton signals.

(d) *2-Methoxy-4-phenylflavane (9).* This compound, m.p. 107 °C (methanol), was prepared from 3-(o-hydroxyphenyl)-3-phenylpropiophenone according to Holmberg and Axberg.[18] The reaction of *9* with 70 % perchloric acid in glacial acetic acid solution carried out as mentioned above gave 4-phenylflavylium perchlorate (*3*) (90 % yield) and *cis*-4-phenylflavane (*2*) (90 % yield). With TFA, *cis*-4-phenylflavane (*2*) separated in 90 % yield and subsequent treatment with a mixture of 70 % perchloric

and acetic acids (1:10) gave 4-phenylflavylium perchlorate (*3*) in 90 % yield.

(e) *3-(Flav-2-ene-4-yl)-2-methoxyflavane (10).* This compound, m.p. 204 °C (methanol) was prepared from flavylium perchlorate (*7*) and sodium borohydride in methanol according to VanAllan and Reynolds.[2] The ¹H NMR spectrum of a solution of *10* in TFA showed the characteristic signals of the flavylium cation *7*, and flavane (*6*), besides, a singlet due to a methoxy group. The band integration was consistent with a 3:1 ratio between *7* and *6*. GLC analysis confirmed the presence of the flavane (*6*). On addition of a mixture of 70 % perchloric and acetic acids (1:10, 10 ml) followed by ether (100 ml), flavylium perchlorate, m.p. 180 °C, separated out. The reaction of *10* with 70 % perchloric acid in glacial acetic acid solution carried out as mentioned for flav-2-ene afforded flavylium perchlorate (*7*) in approximately 85 % yield.

Reaction of 4-phenylflavylium perchlorate (3) with sodium formate. A solution of 4-phenylflavylium perchlorate (*3*) (0.50 g, 0.0013 mol) in acetonitrile (10 ml) was refluxed with sodium formate (0.40 g, 0.006 mol) for 10 h. Ether (100 ml) was added and the precipitate was filtered off. The crystalline residue (0.36 g, 97 % yield) obtained after evaporation of the filtrate was dissolved in deuteriochloroform. The ¹H NMR spectrum of this solution showed the characteristic signals of the H$_\beta$ H$_\gamma$ protons of *1* and the H$_\alpha$, H$_\beta$ protons of *11*, besides the aromatic proton signals. The integral ratio revealed a 1:1 mixture of the flavenes.

Reaction of flavylium perchlorate (7) with sodium formate. A solution of flavylium perchlorate (*7*) (1 g, 0.0033 mol) in acetonitrile (10 ml) was refluxed with sodium formate (0.70 g, 0.01 mol) for 5 h. GLC analysis of the solution showed the presence of flav-2-ene (*5*). Ether (100 ml) was added and the precipitated salts were filtered off. The filtrate after evaporation gave flav-2-ene (*5*) (0.6 g, 90 % yield) identified by ¹H NMR.

Reaction of 4-phenylflav-2-ene (1) with formic acid. A solution of *1* (1 g, 0.0035 mol) in anhydrous formic acid (20 ml) was refluxed for 7 h and then kept at room temperature overnight. *cis*-4-Phenylflavane (*2*), m.p. 144 °C, which separated was filtered (0.45 g, 90 % yield). The filtrate was evaporated and the residue was dissolved in deuteriochloroform. The ¹H NMR spectrum of this solution showed the characteristic singlet of the H$_\beta$ proton of the 4-phenylflavylium cation (*3*), together with its aromatic proton multiplet. Signals due to the flavenes *1* or *11* could not be detected. On addition of a mixture of 70 % perchloric and acetic acids (1:10, 10 ml) followed by ether (100 ml), 4-phenylflavylium perchlorate (*3*), m.p. 222 °C, separated and was filtered off (0.45 g, 70 % yield).

The above experiment was repeated and after isolation of *cis*-4-phenylflavane (*2*) (0.43 g),

the filtrate was evaporated and the residue was refluxed in acetonitrile (15 ml) for 5 h. The crystalline residue (0.5 g) obtained after evaporation of the solvent was 1:1 mixture (^{1}H NMR) of 4-phenylflav-2-ene (*1*) and 4-phenylflav-3-ene (*11*).

Reaction of flav-2-ene (5) with formic acid. A solution of flav-2-ene (*5*) (0.50 g, 0.0024 mol) in anhydrous formic acid (10 ml) was refluxed for 10 h. GLC analysis showed the presence of flavane (*6*) which was obtained in 80 % yield (0.4 g) as an oil after evaporation of the solution.

Reaction of flavylium perchlorate (7) with 4-phenylflav-2-ene (1). A solution of flavylium perchlorate (*7*) (0.22 g, 0.0007 mol) and 4-phenylflav-2-ene (*1*) (0.20 g, 0.0007 mol) in acetonitrile (8 ml) was stirred at 20 °C for 2 h. On addition of ether (100 ml), 4-phenylflavylium perchlorate (*3*) (0.22 g), m.p. 222 °C, separated and was filtered off. Evaporation of the filtrate afforded flav-2-ene (0.15 g).

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