

Intermolecular Hydride Transfer Reactions. III. Reactions of 1,1-Diarylethylenes with Flavylium Perchlorate, 2,6-Dimethoxycarbonylpyrylium Perchlorate and 2,6-Dimethoxycarbonyl-4H-pyran

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The reaction of flavylium perchlorate with 1,1-di(*p*-methoxyphenyl)ethylene to yield 4-[2,2-di(*p*-methoxyphenyl)vinyl]flavylium perchlorate has been reinvestigated. Formation of 1,1-di(*p*-methoxyphenyl)ethane was observed in addition to the flavylium salt. The reaction of 2,6-dimethoxycarbonylpyrylium perchlorate with 1,1-diarylethylenes resulted in the corresponding 4-vinyl substituted pyrylium salts. Treatment of 2,6-dimethoxycarbonyl-4H-pyran and 1,1-di(*p*-methoxyphenyl)ethylene with perchloric acid yielded 4-[2,2-di(*p*-methoxyphenyl)vinyl]2,6-dimethoxycarbonylpyrylium perchlorate and 1,1-di(*p*-methoxyphenyl)ethane. Electrophilic substitutions and intermolecular hydride transfer reactions accounted for the observed products.

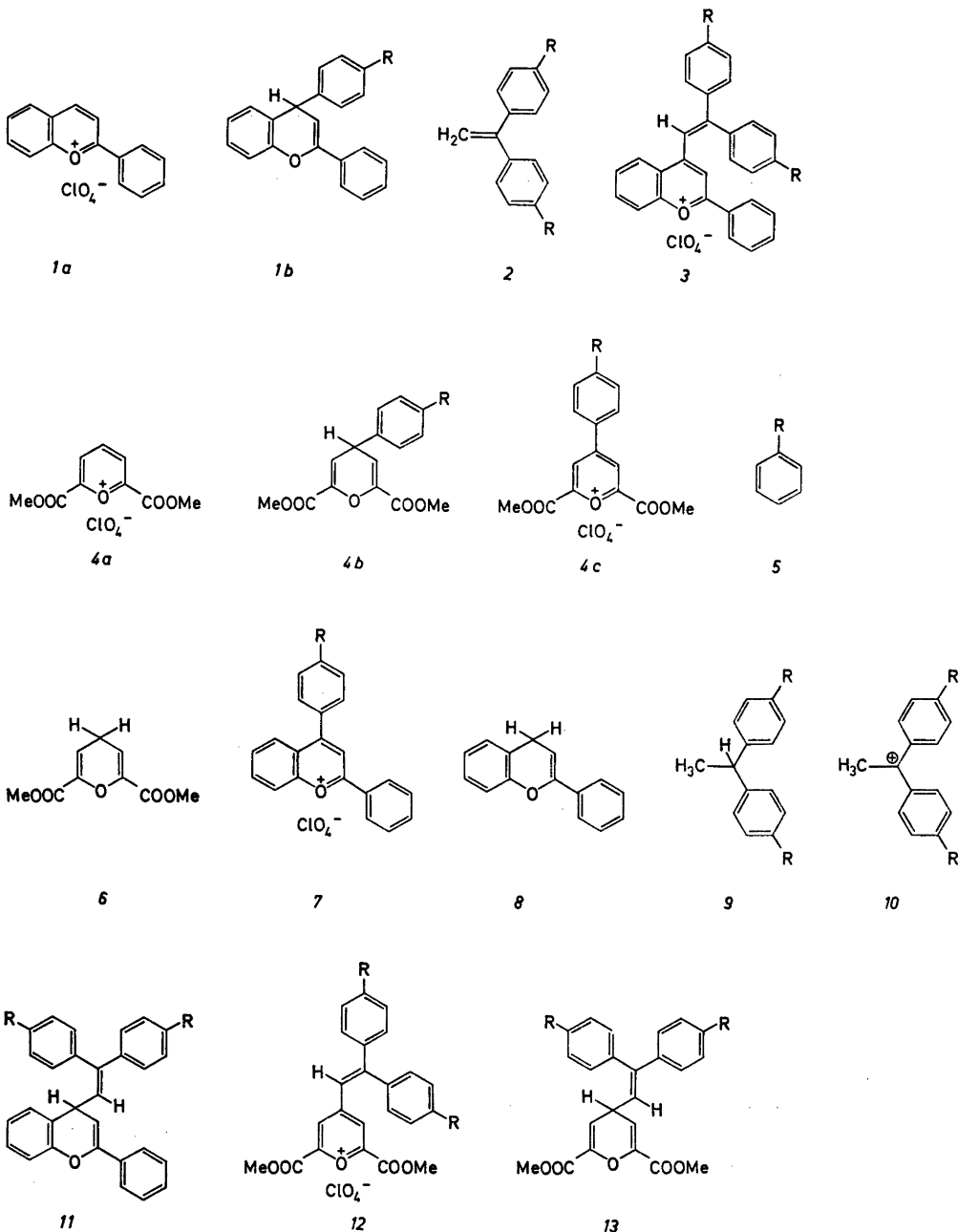
The reactions of flavylium perchlorate (*Ia*) with 1,1-diarylethylenes *2* have been studied by Wizinger *et al.*¹ Dehydrogenated adducts (*3*) were reported to be formed. The fate of the missing hydrogen atoms was not explained (Scheme 1A).

Recently examples of intermolecular hydride transfer reactions leading to related adducts have been studied. These are summarized in Scheme 1B,C. 2,6-Dimethoxycarbonylpyrylium perchlorate (*4a*) was shown to react with mono-substituted benzene derivatives *5* (R = Me, OMe, N(Me)₂) leading to the introduction of the 4H-pyranyl group into the *para* position of *5*. The 4H-pyranyl group was further oxidized into the corresponding pyrylium cation by intermolecular hydride transfer reaction. The pyrylium cation *4a* which acted as hydride acceptor was

reduced to the 4H-pyran *6*.² Similar reactions between the flavylium perchlorate (*Ia*) and dimethylaniline (*5*, R = N(Me)₂) yielded the dehydrogenated adduct *7* (R = N(Me)₂) and the parent flavene *8*.³

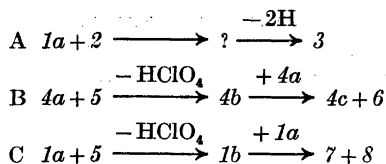
Considering the flavylium cation *Ia* as a potential hydride acceptor, it was felt that similar intermolecular hydride transfer may be involved in the formation of the dehydrogenated adducts *3* (eqn. I, Table 1).

The reaction of flavylium perchlorate (*I*) with dianisylethylene (*2*, R = OMe) in boiling acetic acid solution was repeated¹ and after concentration of the reaction mixture the residue was triturated with ether. The ether insoluble material was removed by filtration. However, the expected flavene *8* could not be detected by ¹H NMR or GLC of the concentrated ether solution. The ¹H NMR spectrum of the residual oil showed a doublet centered at δ 1.6 (*J* 7.5, 3 H), a singlet at δ 3.7 (6 H), a quartet centered at δ 4.0 (*J* 7.5, 1 H) and the usual pattern due to a *para*-substituted benzene derivative centered at δ 7.0 (8 H). The spectrum suggested that dianisylethane (*9*, R = OMe) was formed, the presence of which was further verified by GLC. A possible explanation for the formation of *9* (R = OMe) and the dehydrogenated adduct *3*, is given in Scheme 2A,B. Considering the first step as a substitution reaction, perchloric acid will be liberated. Protonation of unreacted dianisylethylene (*2*, R = OMe) would give the

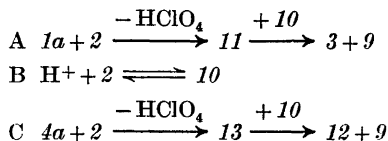


carbonium ion **10** ($R = \text{OMe}$) which subsequently oxidizes the substitution product **11** ($R = \text{OMe}$) to yield the dehydrogenated adduct **3** ($R = \text{OMe}$) and the reduction product **9** ($R = \text{OMe}$) by hydride transfer. Nearly equimolecular amounts

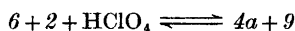
of **1a** and **2** ($R = \text{OMe}$) were used in this reaction. According to the steps outlined above, only 50 % of the substrate **1a** should be transformed into **3** ($R = \text{OMe}$) assuming a quantitative reaction. The ether insoluble material from the



Scheme 1.

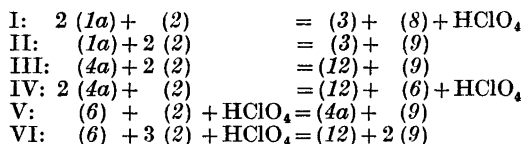


Scheme 2.



Scheme 3.

Table 1. Eqns. I–VI.



above reaction was dissolved in trifluoroacetic acid. The 1H NMR spectrum of this solution indicated a mixture of **3** (R=OMe) and the substrate **1a**. Only traces of unreacted dianisylethylene (**2**, R=OMe) could be identified from analysis of the ether soluble and insoluble fractions.

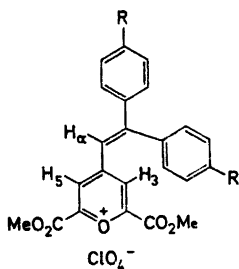
When the reaction was repeated with **1a** and **2** (R=OMe) in molar ratio 1:2, respectively, the dehydrogenated adduct **3** (R=OMe) was formed in a yield corresponding to 93 % transformation of substrate **1a** into **3** (R=OMe). Dianisylethane (**9**, R=OMe) was the only reduction product which could be identified. The stoichiometry of the reaction is given by eqn. II, Table 1.

Similar reactions were carried out between the pyrylium salt **4a** and the diphenylethylenes **2** (R=H, Me, OMe) in acetonitrile solution at 20 °C using molar ratio 1:2, respectively. Pyrylium salts **12** (R=H, Me, OMe) were isolated in high yields and the reduction products **9** (R=H, Me, OMe) were identified (Scheme 2B,C). The stoichiometry of the reaction is given by eqn. III, Table 1.

The reaction of **4a** with dianisylethylene (**2**, R=OMe) in the molar ratio 2:1, respectively, was studied in trideuterioacetonitrile solution (eqn. IV, Table 1). 1H NMR analysis of the reaction mixture clearly established the formation of the dehydrogenated adduct **12** (R=OMe) and the 4H-pyran **6**. Furthermore signals due to dianisylethane **9** (R=OMe) and unreacted pyrylium salt **4a** were observed. Formation of **6** and **9** (R=OMe) indicated hydride transfer both to the pyrylium salt **4a** and to the carbonium ion **10** (R=OMe). With two hydride acceptors present in the reaction between **4a** and **2** (R=OMe), both possibly capable of oxidizing the substitution product **13** (R=OMe), the redox reaction depicted in Scheme 3 had to be considered (eqn. V, Table 1). The 1H NMR spectrum of dianisylethylene (**2**, R=OMe) in deuteriochloroform solution showed a singlet at δ 5.3 (2 H), a singlet at δ 3.8 (6 H) and the pattern due to the aromatic protons centered at δ 7.1 (8 H). In trifluoroacetic acid solution the aromatic and the methoxy proton signals were shifted downfield to δ 7.8 (8 H) and δ 4.2 (6 H), respectively. A singlet at δ 3.3 (3 H) was interpreted as being due to the methyl group of the carbonium ion **10** (R=OMe) but no signal due to the ethylenic protons was observed (Scheme 2B). The downfield shifts mentioned above supported the idea of the electron deficient species. In deuteriotrifluoroacetic acid solution the singlet at δ 3.3 could not be detected. Only signals due to the methoxy groups and the aromatic protons were observed. This indicates that complete deuterium incorporation had taken place in the methyl group of **10** (R=OMe) during the preparation of the sample. The exchanged protons appeared as a singlet at δ 11.4, which is the normal shift position of trifluoroacetic acid. The deuterium/hydrogen exchange is supposed to take place through the equilibrium given in Scheme 2B. Furthermore, it is assumed that the concentration of **2** (R=OMe) in trifluoroacetic acid solution is low, since its presence was not detectable in the 1H NMR spectrum of the equilibrium mixture. When an equimolecular amount of the 4H-pyran **6** was added to the solution of **2** (R=OMe) in trifluoroacetic acid, the 1H NMR spectrum showed that the redox reaction corresponding to the reaction given in Scheme 3 was displaced to the right. However, it should

be pointed out that the observed signals were due to dianisylethane (*9*, R=OMe) and the cation *12* (R=OMe). The formation of the latter compound suggests that the pyrylium cation *4a* formed, immediately reacts with *2* corresponding to the reaction given in Scheme 2C. The observation of signals due to unreacted 4*H*-pyran *6*, supported this conclusion.

The above mentioned conclusion indicates that a reaction between one mol of the 4*H*-pyran *6* and three mol of dianisylethylene (*2*, R=OMe) in acidic solution would be expected to proceed quantitatively into the pyrylium cation *12* (R=OMe) and dianisylethane *9* (R=OMe). One mol of *6* and one mol of *2* (R=OMe) should give one mol of pyrylium cation *4a* according to Scheme 3 and the additional two mol of *2* (R=OMe) should give the pyrylium cation *12* (R=OMe) according to Scheme 2C. Evidently, the ¹H NMR spectrum of this reaction mixture in trifluoroacetic acid after 4 days at 20 °C exhibited mainly signals due to the pyrylium cation *12* (R=OMe) and dianisylethane (*9*, R=OMe). Furthermore the pyrylium salt *12* (R=OMe) was obtained in 90 % yield from a reaction carried out in a mixture of acetic acid and perchloric acid. The yield was calculated according to eqn. VI, which is the sum of eqns. V and III (Table 1).



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Table 2. ¹H NMR spectra of pyrylium perchlorate *12* in TFA (δ).

R	H ₅	H ₃	H _{α}	H _{Ar}	R	CO ₂ Me
H	8.05 ^a	8.05 ^a		7.3 – 7.9 ^{b,c}		4.13 ^a
Me	7.90 ^a	7.90 ^a	7.66 ^{a,c}	7.3 – 7.7 ^{b,c}	2.21 ^a	4.13 ^a
OMe	7.65 ^{a,c}	7.65 ^{a,c}	7.49 ^a	7.3 ^d , 7.7 ^{d,c}	4.10 ^{a,c}	4.10 ^{a,c}

^a singlet. ^b multiplet. ^c superimposed. ^d AA'BB' system, $J_{AB} = 9.0$ Hz.

The 4*H*-pyran *6* was not identified from reactions carried out between the pyrylium cation *4a* and dianisylethylene (*2*, R=OMe) in 1:2 ratio. Direct hydride transfer from the substitution product to the protonated dianisylethylene *10* (R=OMe) accounted for the observed products *12* (R=OMe) and *9* (R=OMe) (eqn III, Table 1). However, since eqn. III is the sum of IV and V, it seems possible that hydride transfer to the pyrylium salt *4a* may occur to some extent with formation of *6* which is subsequently reoxidized through a second hydride transfer (eqn. V). This may explain the formation of only reduction product *9* (R=OMe). Kinetic studies of these reactions have not been carried out. The intermediate substitution product *11* and *13* could not be detected from the reactions between the heterocyclic cations *1a*, *4a*, and dianisylethylene (*2*, R=OMe). This indicates that the hydride transfer reactions are faster than the substitution reactions. Furthermore, it should be pointed out that in the hydride transfer between the substitution products and the cation *10* (R=OMe), two tertiary carbon atoms are involved. In hydride transfer reactions between the substitution products and the heterocyclic cations and in redox reactions as shown in Scheme 3, tertiary and secondary carbon atoms are involved. With respect to sterical effects, it seems likely that the latter examples of hydride transfer reactions should be favoured.

The ¹H NMR shift values of the pyrylium salt *12* are listed in Table 2.

The increased stabilizing effect of substituent R on the pyrylium cation through the series H, Me, OMe is reflected in chemical shift positions of the heterocyclic ring protons. The upfield shifts of these protons are in agreement with a

decreased positive charge of the pyrylium nucleus.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian A-60A instrument. A Perkin-Elmer F-11 instrument equipped with an OV-17 column was used for GLC analysis.

4-[2,2-Di(*p*-methoxyphenyl)vinyl]flavylium perchlorate (3, $R = \text{OMe}$)¹ and 1,1-di(*p*-methoxyphenyl)ethane (9, $R = \text{OMe}$). A mixture of flavylium perchlorate (1a)⁴ (1.53 g, 0.005 mol) and 1,1-di(*p*-methoxyphenyl)ethylene (2, $R = \text{OMe}$)⁵ (2.4 g, 0.01 mol) in acetic acid solution (100 ml) was refluxed for 12 h. The precipitated material was collected by filtration after 24 h and washed with dry ether. The yield of 3 ($R = \text{OMe}$) was 2.48 g (93%), m.p. 237 °C (decomp.), λ_{max} 568 nm (AcOH). ^1H NMR spectrum of 3 ($R = \text{OMe}$) (trifluoroacetic acid solution): δ 4.08 (6 H, s), 7.7–8.3 (19 H, m). The filtrate was evaporated and the residue was extracted with ether (200 ml). The ether solution was concentrated and 9 ($R = \text{OMe}$) was identified by the ^1H NMR spectrum of the residual oil in deuteriochloroform solution: δ 1.58 (*J* 7.5 Hz, 3 H, d), 3.75 (6 H, s), 4.05 (*J* 7.5 Hz, 1 H, q), 6.8 (J_{AB} 9.0, 8 H, AA'BB'-system). Authentic samples of 9 ($R = \text{OMe}$)⁶ and 2-flavene (8)⁷ were prepared for purposes of identification. GLC analysis verified the formation of 9 ($R = \text{OMe}$). The flavene 8 could not be detected.

4-(2,2-Diarylvinylyl)-2,6-dimethoxycarbonylpyrylium perchlorate (12) and 1,1-diarylethane (9). *General procedure.* 2,6-Dimethoxycarbonylpyrylium perchlorate (4a)⁸ (0.0025 mol) was added to a solution of 1,1-diarylethylene (2) (0.005 mol) in dry acetonitrile (25 ml) at 20 °C. After stirring for 24 h the solution was evaporated. The residue was triturated with ether (500 ml). The pyrylium salt 12 was collected by filtration and recrystallized from acetic acid. The filtrate was evaporated and the residue was examined by ^1H NMR spectroscopy for reduction products.

4-[2,2-Di(*p*-methoxyphenyl)vinyl]-2,6-dimethoxycarbonylpyrylium perchlorate (12, $R = \text{OMe}$) was prepared from the pyrylium salt 4a and 1,1-di(*p*-methoxyphenyl)ethylene (2, $R = \text{OMe}$)⁵ in 90% yield, m.p. 140 °C (decomp.), λ_{max} 580 nm (AcOH). ^1H NMR spectrum, see Table 2. (Found: C 56.01; H 4.39; Cl 6.82. Calc. for $\text{C}_{28}\text{H}_{28}\text{O}_{11}\text{Cl}$: C 56.13; H 4.30; Cl 6.64).

1,1-Di(*p*-methoxyphenyl)ethane (9, $R = \text{OMe}$) was identified from the reaction of 4a with 2 ($R = \text{OMe}$). ^1H NMR spectrum (CDCl_3): δ 1.58 (*J* 7.5 Hz, 3 H, d), 3.75 (6 H, s), 4.05 (*J* 7.5 Hz, 1 H, q), 6.8 (J_{AB} 9.0 Hz, 8 H, AA'BB'-system).

4-(2,2-Diphenylvinyl)-2,6-dimethoxycarbonylpyrylium perchlorate (12, $R = \text{H}$) was prepared from the pyrylium salt 4a and 1,1-diphenylethylene (2, $R = \text{H}$) in 70% yield, m.p. 186 °C

(decomp.), λ_{max} 493 nm (AcOH). ^1H NMR spectrum, see Table 2. (Found: C 58.08; H 4.11. Calc. for $\text{C}_{28}\text{H}_{19}\text{O}_9\text{Cl}$: C 58.16; H 4.00).

1,1-Diphenylethane (9, $R = \text{H}$) was identified from the reaction of 4a with 2 ($R = \text{H}$) by comparison with a sample prepared from catalytic hydrogenation of 2 ($R = \text{H}$) in ethyl acetate (10% Pd/CaCO₃). ^1H NMR spectrum (CDCl_3): δ 1.58 (*J* 7.5 Hz, 3 H, d), 4.08 (*J* 7.5 Hz, 1 H, q), 7.17 (10 H, narrow m).

4-[2,2-Di(*p*-methylphenyl)vinyl]-2,6-dimethoxycarbonylpyrylium perchlorate (12, $R = \text{Me}$) was prepared from the pyrylium salt 4a and 1,1-di(*p*-methylphenyl)ethylene (2, $R = \text{Me}$)⁵ m.p. 178 °C (decomp.). ^1H NMR spectrum, see Table 2. (Found: C 59.52; H 4.50. Calc. for $\text{C}_{28}\text{H}_{23}\text{O}_9\text{Cl}$: C 59.70; H 4.58).

1,1-Di(*p*-methylphenyl)ethane (9, $R = \text{Me}$) was identified from the reaction of 4a with 2 ($R = \text{Me}$) by comparison with a sample prepared from catalytic hydrogenation of 2 ($R = \text{Me}$) in ethyl acetate (10% Pd/CaCO₃, 3 atm.). ^1H NMR spectrum (CDCl_3): δ 1.58 (*J* 7.5 Hz, 3 H, d), 2.29 (6 H, s), 4.05 (*J* 7.5 Hz, 1 H, q), 7.1 (8 H AA'BB'-system).

4-[2,2-Di(*p*-methoxyphenyl)vinyl]-2,6-dimethoxycarbonylpyrylium perchlorate (12, $R = \text{OMe}$). 2,6-Dimethoxycarbonyl-4H-pyran (6)⁸ (0.495 g, 0.0025 mol) and 1,1-di(*p*-methoxyphenyl)ethylene (2, $R = \text{OMe}$)⁵ (1.8 g, 0.0075 mol) were added to a mixture of acetic acid (50 ml) and 70% perchloric acid (0.5 g). The reaction mixture was left at 25 °C for 4 days with stirring, diluted with ether (300 ml) and after 12 h the precipitated material was collected by filtration. Yield 90% (1.2 g), m.p. 140 °C (decomp.), λ_{max} 580 nm (AcOH), ^1H NMR spectrum, see Table 2.

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REFERENCES

1. Wizinger, R. and Luthiger, A. *Helv. Chim. Acta* 36 (1953) 526.
2. Østensen, E. T. *Acta Chem. Scand. B* 28 (1974) 1107.
3. Østensen, E. T. *Acta Chem. Scand. B* 29 (1975) 787.
4. Wizinger, R. and v. Tobel, H. *Helv. Chim. Acta* 40 (1957) 1305.
5. Pfeiffer, P. and Wizinger, R. *Justus Liebigs Ann. Chem.* 461 (1928) 132.
6. Hoffenberg, D. S., Smolin, E. M. and Matsuda, K. *J. Chem. Eng. Data* 9 (1964) 104.
7. Freudenberg, K. and Weinges, K. *Justus Liebigs Ann. Chem.* 590 (1954) 140.
8. Undheim, K. and Østensen, E. T. *Acta Chem. Scand.* 27 (1973) 1385.

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