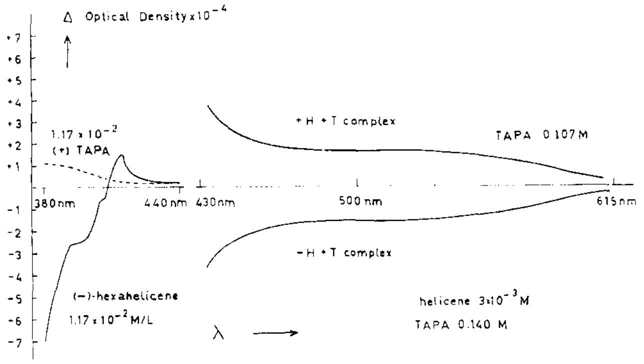
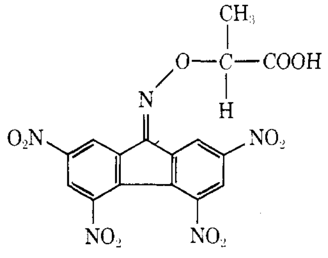


Figure 1.

**Chart I**

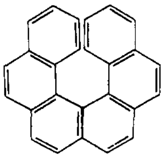
Acceptor



I

(+)-TAPA

Donor



II

Complex

$$A_+ + D_+ \overset{K_-}{\rightleftharpoons} A_+D_+$$

$$A_+ + D_- \overset{K_-}{\rightleftharpoons} A_+D_-$$

(+)-hexahelicene ⟶ $K_+ = 4.6$

(−)-hexahelicene ⟶ $K_- = 5.5$

enantiomer which complexes poorest with (+)-TAPA crystallizes from solution. Although no spectral data of these complexes have been recorded, it has been noted[12] that solutions become deeply colored. Naturally the successful resolution itself is strong supportive evidence for the hypothesis that indeed the diastereomeric CT complexes have different equilibrium constants.

When (+)-hexahelicene ($[\alpha]^{20}{}_{578}$ +2717°; $CHCl_3$) and (+)-TAPA ($[\alpha]^{20}{}_{578}$ = +80°; $CHCl_3$) were mixed in chloroform and the circular dichroism of the resulting solution was recorded, the spectrum shown in Figure 1 was obtained. A broad positive CD band with a maximum at 510 nm is observed.

Neither (+)- nor (−)-hexahelicene nor (+)-TAPA separately exhibit circular dichroism between 430 and 600 nm (see Figure 1 for the CD spectra of the individual components). A comparison with the CD spectrum (Figure 1) obtained from the diastereomeric complex, namely the complex from (−)-hexahelicene ($[\alpha]^{20}{}_{578}$ −3016°; $CHCl_3$) and (+)-TAPA ($[\alpha]^{20}{}_{578}$ +80°; $CHCl_3$) is instructive. Again a broad absorption band is observed at 510 nm. It is clear that the two diastereomeric complexes have charge-transfer bands at the same wavelength and that their rotational strengths are slightly different in magnitude and opposite in sign. The observation that these diastereomeric complexes furnish CD spectra in the CT region which are nearly mirror images of one another suggests strongly that the donor component (in this case (+)- and (−)-hexahelicene) dominates the sign of the ellipticity.

Both CD spectra show a second absorption band up to 430 nm, having the same sign of rotational strength as the band at 510 nm. This second absorption at the end of the spectrum could not be detected entirely. This band might be attributed to a second charge-transfer absorption. The equilibrium constant of each complex was determined with circular dichroism using the equation

$$O/[D]_0[A]_0 = K[O_m - (O/[D]_0)]$$

for $[A]_0 \gg$ [complex]. When $D + A \rightleftarrows DA$, $K_+$ is the equilibrium constant for the (+)-hexahelicene–(+)-TAPA and $K_-$ for the (−)-hexahelicene–(+)-TAPA complex. $O$ is the area under the charge-transfer absorption band. $O_m$ is the maximum area for $s = 1$, where $s = [\text{complex}]/[D]_0$. Instead of the area under the band the difference in optical density at various wavelengths can also be used. $\pm[D]_0$ and $+[A]_0$ are the original donor and acceptor concentrations. The following data were found: $K_+ = 4.6$ with $s = 0.45$ and $K_- = 5.5$ with $s = 0.51$. The accuracy of these data was secured by determining the sum of the equilibrium constants of the two complexes using ultraviolet spectroscopy.[8] A modified Scatchard equation was used, with the necessary condition that the racemic component must be in excess. With $K_{tot} = \Sigma_i K_i$ and $\epsilon_{eff} = \Sigma_i K_i \epsilon_i / \Sigma_i K_i$ this gives $E/0.5[D]_0[A]_0 = K_{tot}[\epsilon_{eff} - (E/[A]_0)]$; $[D]_0$ is in excess. $E$ is the absorbance of the complexes and $\epsilon_{eff}$ is the effective extinction coefficient. The following data were obtained: $K_{tot} = 10.0$ and $\epsilon_{eff} = 830$ with $s = 0.63$. This means that the $K_+$ and $K_-$ are in good agreement with the determined $K_{tot}$, although these values were obtained with different techniques and under different conditions.

It appears safe to conclude that—at least for the case at hand—diastereomeric charge-transfer complexes have significantly different physical properties and that a careful study of the CD spectra of CT bands of chiral acceptors (donors) and chiral natural products might provide useful information.

**Acknowledgment.** We thank Dr. Jan Verhoeven of the University of Amsterdam for helpful discussions.

**Hans Wynberg,* Koop Lammertsma**
*Department of Organic Chemistry, The University*
*Groningen, The Netherlands*

*Received June 18, 1973*

---

## Photochemical Rearrangements of Neutral and Protonated 4-Pyrones

*Sir:*

The photochemistry of 4-pyrones has been shown to be remarkably dependent on the number of substituents present in the pyrone ring. Thus although the dimerization of 2,6-disubstituted-4-pyrones is a well-documented photochemical reaction,[1,2] Ishibi has

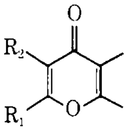
---

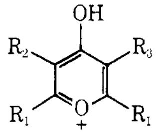
(1) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **80**, 6150 (1958).

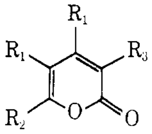
(2) N. Sugiyama, Y. Sato, and C. Kashirma, *Bull. Chem. Soc. Jap.*, **43**, 3205 (1970).

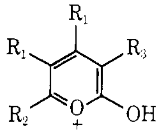
recently observed that 3,5-diphenyl-2,6-disubstituted-4-pyrones undergo photoisomerization to 3,6-diphenyl-4,5-disubstituted-2-pyrones.[3,4] Interestingly, however, these same workers report that trisubstituted-4-pyrone. 3-phenyl-2,6-dimethyl-4-pyrone, undergoes neither dimerization nor isomerization but is unaffected by irradiation.[4]

In order to gain insight into the nature of the excited states involved in these reactions, we have investigated the photochemistry of 4-hydroxypyrylium cations **2a–c** in 96% $H_2SO_4$[5] and of neutral 4-pyrones **1a–c** in solvents of varying polarity. We wish to report that these 4-hydroxypyrylium cations undergo photoisomerizations to yield 2-hydroxypyrylium cations as the major or only detectable products. Similarly, irradiation of neutral 4-pyrones **1a–c** yielded the respective 2-pyrones **3a–c** in a rearrangement that is accelerated by increasing solvent polarity.


1


2


3


4

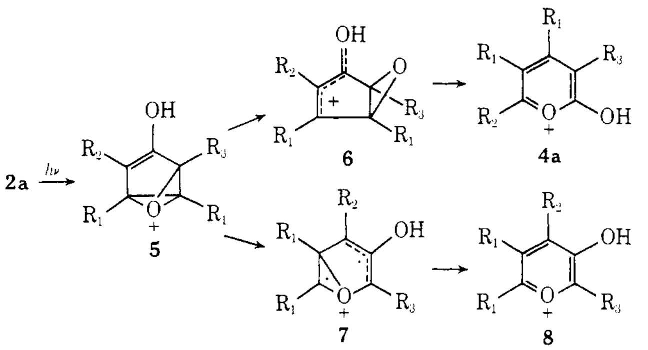
a, $R_1 = CH_3$; $R_2 = R_3 = Ph$
b, $R_1 = CH_3$; $R_2 = Ph$; $R_3 = H$
c, $R_1 = R_2 = R_3 = CH_3$

Photolyses of **2a**, **2b**, and **2c** at 2537 Å (1 × $10^{-2}$ *M* in 96% $H_2SO_4$) were monitored by uv–visible absorption spectroscopy.[6] Neutralization and extraction of the resulting solutions led to the isolation by silica gel column chromatography of the respective 2-pyrones **3a**, **3b**, and **3c** in yields of 68, 40, and 87%, respectively.[7]

In the case of **2a**, in addition to the absorption bands associated with **4a**, an additional product absorbing at 530 and 442 nm was observed after short duration irradiation. Although the spectrum of this solution did not change after prolonged standing in the dark, continued irradiation at either 254 or 530 nm resulted in the loss of these long wavelength bands without significant change in the optical densities at 345, 248, or 221 nm. Furthermore, since **4a** is both photochemically and thermally stable under these conditions, this additional product is neither an intermediate in the formation of **4a** nor is it formed from it. Upon neutralization, this additional photoproduct is apparently also converted to 2-pyrone **3a** since the yields of **3a** obtained from $H_2SO_4$ solutions neutralized prior to the destruction of the 530 nm absorption were consistently 10–15% higher than the yields from solutions neutralized after prolonged irradiation had destroyed this absorption peak.

On the basis of these observations we suggest that this additional photoproduct is 3-hydroxypyrylium cation, **8**.[9] By analogy with the thermal tautomerism of tetraphenylpyrylium 3-oxide,[10] upon neutralization, **8** might be expected to yield its valence tautomer, the conjugate base of **6**, which could readily isomerize to **3a**. Although one could envision both **4a** and **8** arising from the same precursor, namely **6** in Scheme I, their greatly differing rates of formation suggest that this is not the case. Thus when a 5 × $10^{-5}$ *M* solution of **2a** was spectroscopically monitored at 530 nm immediately following a 10 sec irradiation, the optical density was observed to have increased from 0 to 0.01 during photolysis and from 0.01 to 0.54 during the following 250 sec dark period. Conversely, however, when an identically irradiated solution was monitored at 342 nm immediately following irradiation, the optical density increased from 0 to 0.29 during irradiation but remained constant during the subsequent dark period.

**Scheme I**



A plausible mechanism which accounts for these observations is shown in Scheme I. Oxaniabenzvalene cation, **5**, formed upon $\pi,\pi^*$ excitation of **2a** could undergo 1,6 or 2,3 bond fission to give **6** or **7**, respectively. Although epoxycyclopentenones are known to undergo rapid acid catalyzed rearrangement to 2-pyrones,[11,12] the isomerization of **7** to **8** might be anticipated to take place more slowly. In addition to the stability of **7** imparted by delocalization of the odd electron throughout the phenyl groups $R_2$ and $R_3$, conversion to **8** requires disrotatory opening of the 1,5 bond, symmetry forbidden in the ground state of **7**. An intermediate analogous to **7** has recently been suggested by Barltrop and his colleagues to result from photolysis of trialkylpyrylium salts in aqueous solution.[13] Although in the latter case the intermediate was suggested as a precursor to an oxaniabenzvalene cation, the present scheme requires the reverse to be true.[14]

---

[3] N. Ishibi, M. Odani, and M. Sunami, *Chem. Commun.*, 1034 (1971).

[4] N. Ishibi, M. Sunami, and M. Odani, *J. Amer. Chem. Soc.*, **95**, 463 (1973).

[5] For a previous report on the photochemistry of 4-hydroxypyrylium cations see J. W. Pavlik and E. L. Clennan, *J. Amer. Chem. Soc.*, **95**, 1697 (1973).

[6] Cation **2a** $\lambda_{max}$ 225 ($\epsilon$ 18,600), 290 nm (s, $\epsilon$ 5800); cation **4a** $\lambda_{max}$ 345 ($\epsilon$ 14,600), 248 ($\epsilon$ 9600), 221 nm ($\epsilon$ 15,000); cation **2b** $\lambda_{max}$ 227 ($\epsilon$ 13,800), 257 nm ($\epsilon$ 9400); cation **4b** $\lambda_{max}$ 335 ($\epsilon$ 12,800), 243 ($\epsilon$ 6600), 219 nm ($\epsilon$ 13,300); cation **2c** $\lambda_{max}$ 268 ($\epsilon$ 12,800), 244 nm ($\epsilon$ 8000); cation **4c** $\lambda_{max}$ 306 ($\epsilon$ 18,600), 226 nm ($\epsilon$ 3600).

[7] **3a** was identical with the product isolated by Ishibi;[4] **3b**, mp 103° (lit.[8] 101–102); ir ($CCl_4$) 3260, 2920, 1725, 1630, 1440, 1390, 1380, 1200, 1080, 1065 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 7.3–7.6 (m, 5 H), 6.0 (s, 1 H), 2.03 (s, 3 H), 2.15 (s, 3 H); mass spectrum (70 eV) at *m/e* (relative intensity, %): 200 (70), 172 (100), 157 (7), 143 (26), 105 (22), 77 (40), 67 (10); **3c**, mp 46–47°; ir ($CCl_4$) 2930, 1710, 1650, 1385, 1210, 1190, 1085 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 2.27 (s), 2.30 (s), 2.40 (s), 2.53 (s); mass spectrum (70 eV) at *m/e* (relative intensity, %) 152 (66), 124 (100), 123 (79), 109 (90), 81 (47), 53 (19), 43 (60), 41 (28), 38 (26).

[8] G. Ciamician and P. Silber, *Chem. Ber.*, **27**, 846 (1894).

[9] Ishibi[4] has also observed 3-pyrylium oxides as minor products from photolysis of 4-pyrones.

[10] J. M. Dunston and P. Yates, *Tetrahedron Lett.*, 505 (1964).

[11] R. Pütter and W. Dilthey, *J. Prakt. Chem.*, **119**, 183 (1937); **150**, 40 (1938).

[12] E. F. Ullman, *J. Amer. Chem. Soc.*, **85**, 3529 (1963).

[13] J. A. Barltrop, K. Dawes, A. C. Day, and A. J. H. Summers, *J. Amer. Chem. Soc.*, **95**, 2406 (1973).

[14] Scheme I allows for the formation of two 2-hydroxypyrylium cations from **2b**. Although the broadness of the absorption band at 335 nm formed upon photolysis of **2b** suggested the presence of more than one cation, examination of the crude neutralized product by gc and nmr showed **3b** as the only product formed in greater than trace quantity. Further investigation of this reaction, however, is in progress.

Although it is quite clear that in 96% $H_2SO_4$ isomerization occurs *via* a $\pi,\pi^*$ excited state of **2a**, the nature of the excited states of neutral 4-pyrones has not been established. It seems likely, however, that the similar photoreactivity of **1a** and **2a** also reflects a similarity of their respective excited states. In order to test such a suggestion we have irradiated neutral 4-pyrones **1a** and **1b** in 2,2,2-trifluoroethanol, a highly polar solvent that would be expected to stabilize $\pi,\pi^*$ excited states relative to $n,\pi^*$ excited states.[15]

The relative quantum efficiencies of photoisomerization of **1a** and **1b** in acetonitrile and trifluoroethanol tend to support the suggestion that the isomerization of neutral 4-pyrones also occurs *via* their $\pi,\pi^*$ excited states. Thus irradiation of equimolar solutions of **1a** in acetonitrile and in trifluoroethanol in a merry-go-round apparatus resulted in a 30% greater conversion of **1a** in the latter, more polar solvent. This dependence on solvent polarity was particularly notable in the case of **1b**. Although photostable in acetonitrile,[4] we observe that in trifluoroethanol **1b** is converted to **3b**. These results are inconsistent with the suggestion that the efficiency of the photoisomerization is sterically controlled by the large phenyl groups at positions 3 and 5 of the 4-pyrone ring.[4] Indeed, our observation that tetramethyl-4-pyrone (**1c**) undergoes efficient photoisomerization to **3c** in either acetonitrile or trifluoroethanol clearly shows that phenyl groups in these positions are not a prerequisite to photoisomerization. Rather, these results suggest that the nature of the excited states and hence the reactivity of 4-pyrones is sensitive to the extent of substitution in the 4-pyrone ring.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(15) J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 5296 (1968).

(16) ACS-PRF Undergraduate Research Participant, 1972–1973.

**James W. Pavlik,* Josephine Kwong**[16]
*Department of Chemistry, University of Wisconsin—River Falls*
*River Falls, Wisconsin 54022*

*Received July 11, 1973*

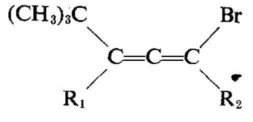
---

## Isotope Effects in the Solvolysis of Haloallenes[1]

*Sir:*

We wish to report the first measurement of an α-secondary isotope effect for an $sp^2$ to sp hybridization change in a solvolysis reaction. We have been examining the behavior of tri- and disubstituted haloallenes under solvolytic conditions.[2] As a mechanistic probe we have measured the α- and β-secondary isotope effects associated with the solvolysis of **1a–e** in aqueous ethanol and trifluoroethanol. These data are collected in Table I.

Data derived from Table I support the proposal that these compounds all react *via* a carbonium ion mechanism.[3] The enhanced reactivity of these haloallenes compared to their vinyl analogs allows the convenient measurement of these rates even though the developing cation is not stabilized by a substituent at the reaction center in **1c**, **d**, and **e**.[4] The solvent dependence of **1a** yields $m = 0.72 \pm 0.05$ at 45°. The temperature dependence data yield the following activation parameters: for **1a** in 70E $\Delta H^{\ddagger} = 22.1$ kcal/mol and $\Delta S^{\ddagger}(25°) = -2.3$ eu, and for **1c** in 70T $\Delta H^{\ddagger} = 21.9$ kcal/mol and $\Delta S^{\ddagger}(25°) = -9.9$ eu. Table II presents the isotope effects observed.



**1a**, $R_1 = CH_3$; $R_2 = (CH_3)_3C$
**b**, $R_1 = CD_3$; $R_2 = (CH_3)_3C$
**c**, $R_1 = CH_3$; $R_2 = H$
**d**, $R_1 = CD_3$; $R_2 = H$
**e**, $R_1 = CH_3$; $R_2 = D$

Table I. Conductometric Rate Constants for Solvolysis of **1**

| Compd | $T$, °C | Solvent[a] | $10^4k$, sec$^{-1}$ [b] |
|---|---|---|---|
| **1a** | 24.62 ± 0.01 | 60E | 3.64 ± 0.06 |
| | | 70E | 1.14 ± 0.02 |
| | 34.68 ± 0.01 | 60E | 12.1 ± 0.1 |
| | | 70E | 4.28 ± 0.03 |
| | | 80E | 1.47 ± 0.02 |
| | 45.30 ± 0.02 | 80E | 5.15 ± 0.04 |
| | | 90E | 1.49 ± 0.03 |
| **1b** | 24.62 ± 0.01 | 60E | 3.10 ± 0.04 |
| | | 70E | 0.98 ± 0.004 |
| | 45.30 ± 0.02 | 80E | 4.31 ± 0.04 |
| | | 90E | 1.22 ± 0.07 |
| **1c** | 50.08 ± 0.01 | 70T | 0.674 ± 0.003 |
| | 60.22 ± 0.01 | | 2.44 ± 0.02 |
| | 70.13 ± 0.01 | | 5.21 ± 0.01 |
| **1d** | 60.24 ± 0.01 | 70T | 2.05 ± 0.002 |
| **1e** | 60.22 ± 0.01 | 70T | 2.03 ± 0.01 |

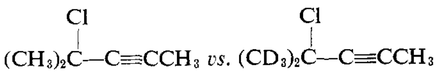
[a] 60E represents 60:40 (v/v) ethanol–water, etc.; 70T represents 70:30 (w/w) trifluoroethanol–water. [b] Average of triplicate determinations.

Table II. Isotope Effects for Solvolysis of **1**

| | $T_1$, °C | Solvent | $k_H/k_D$ (obsd) | $\Delta\Delta F^{\ddagger}$/D[a] | $k_H/k_D$ (calcd)[b] |
|---|---|---|---|---|---|
| **1a/1b** | 24.62 | 60E | 1.17 | 37 | 1.21 ± 0.03 |
| | | 70E | 1.16 | 35 | 1.19 ± 0.02 |
| | 45.30 | 80E | 1.19 | 44 | 1.23 ± 0.02 |
| | | 90E | 1.22 | 50 | 1.27 ± 0.04 |
| **1c/1d** | 60.2 | 70T | 1.19 | 44 | 1.23 ± 0.01 |
| **1c/1e** | 60.2 | 70T | 1.20 | 129 | 1.22 ± 0.01 |

[a] Corrected to 100% deuteration at the temperature of the measurement. (The authors are indebted to Professor Donald Hunt, University of Virginia, for the mass spectral analysis of **1b**, **d**, and **e**.) [b] Calculated from $\Delta\Delta F^{\ddagger}$.

The β-secondary isotope effect observed upon $CD_3$ substitution at the 3 position of a trisubstituted haloallene (**1a**/**1b**) is found to be $k_H/k_D = 1.23$ (44 cal/D) in 80% ethanol at 45°. This is to be compared with that reported by Shiner and Kriz for solvolysis of **2** where



$$(CH_3)_2\overset{Cl}{\overset{|}{C}}\text{—}C\equiv CCH_3 \quad vs. \quad (CD_3)_2\overset{Cl}{\overset{|}{C}}\text{—}C\equiv CCH_3$$

**2**

---

(1) Submitted in partial fulfillment for the degree of Master of Arts in Chemistry, College of William and Mary, 1973.

(2) (a) M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. J. Boswell, *J. Amer. Chem. Soc.*, **93**, 6989 (1971); (b) M. D. Schiavelli, R. P. Gilbert, W. A. Boynton, and C. J. Boswell, *ibid.*, **94**, 5061 (1972); (c) M. D. Schiavelli and P. L. Timpanaro, *J. Org. Chem.*, **38**, 3054 (1973).

(3) It is understood throughout that ion pairs are the most likely candidates for intermediates in these solvolyses. Preliminary results appear to confirm this.

(4) It should be noted that these haloallenes exhibit relative reactivity about one order of magnitude lower than *tert*-butyl chloride and α-phenylethyl chloride and are about as reactive as benzyl halides.