m/z 330.1440, found *m/z* 330.1428.

7-(3-Butynylamino)-2-pivaloyl-6-azapterin (7e). A stirred suspension of **5** (0.58 g, 1.78 mmol) in anhydrous methylene chloride (40 mL) was treated with 4-amino-1-butyne[1e] (0.31 g, 4.49 mmol) at once. The resultant mixture was stirred under nitrogen for 23.5 h. After this period, the reaction mixture was washed with water (2 × 50 mL) followed by brine (1 × 50 mL), dried (anhyd $MgSO_4$), and evaporated under reduced pressure to afford a pale yellow solid. Trituration of this material in ether yielded 7-(3-butynylamino)-2-pivaloyl-6-azapterin (**7e**) as a fine yellow solid (0.50 g, 89%); mp 227–228 °C (effervescent dec); ^1H NMR ($CDCl_3$) δ 12.08 (br s, 1 H), 8.37 (br s, 1 H), 6.83 (br s, 1 H), 3.74 (q, J = 6.4 Hz, 2 H), 2.59 (dt, J_1 = 6.5 Hz, J_2 = 2.6 Hz, 2 H), 2.07 (t, J = 2.7 Hz, 1 H), 1.34 (s, 9 H); HRMS calcd for $C_{14}H_{17}N_7O_2$, *m/z* 315.1443, found *m/z* 315.1426.

Anal. Calcd for $C_{14}H_{17}N_7O_2$: C, 53.33; H, 5.43; N, 31.09. Found: C, 53.13; H, 5.52; N, 31.38.

Intramolecular Diels–Alder Reactions of 7a–e. General Procedure. A suspension of the azapterin **7a–e** in the given solvent (ca 0.2 M) was heated at reflux. The reaction was followed by TLC until completion. The high boiling solvent was removed by fitration of the reaction mixture through a pad of silica gel followed by washing with hexanes; subsequent elution of the silica gel with 1:1 acetonitrile/methylene chloride followed by evaporation under reduced pressure gave the fused 5-deazapterins **8a–e** without further purification (unless otherwise noted).

2-(Pivaloylamino)-3,4,6,7-tetrahydrofuro[3′,2′:5,6]pyrido[2,3-*d*]pyrimidin-4-one (8a): carried out in bromobenzene as solvent for 29 h; white solid, 48% yield; mp 265 °C (slow dec); ^1H NMR ($CDCl_3$) δ 11.94 (br s, 1 H), 8.25 (br s, 1 H), 8.23 (s, 1 H), 4.77 (t, J = 8.6 Hz, 2 H), 3.35 (t, J = 8.4 Hz, 2 H), 1.33 (s, 9 H); HRMS calcd for $C_{14}H_{16}N_4O_3$, *m/z*, 288.1222, found *m/z* 288.1223.

2-(Pivaloylamino)-7-ethyl-3,4,6,7-tetrahydrofuro[3′,2′:5,6]pyrido[2,3-*d*]pyrimidin-4-one (8b): carried out in bromobenzene as solvent for 6 h; white flakes, 65% yield; mp 176–178 °C; ^1H NMR ($CDCl_3$) δ 11.95 (br s, 1 H), 8.32 (br s, 1 H), 8.20 (s, 1 H), 4.98–4.91 (m, 1 H), 3.45–3.37 (m, 1 H), 3.01–2.92 (m, 1 H), 1.99–1.76 (m, 2 H), 1.33 (s, 9 H), 1.07 (t, J = 7.4 Hz, 3 H); HRMS calcd for $C_{16}H_{20}N_4O_3$, *m/z* 316.1535, found *m/z* 316.1519.

Anal. Calcd for $C_{16}H_{20}N_4O_3$: C, 60.75; H, 6.37; N, 17.71. Found: C, 60.52; H, 6.24; N, 17.74.

2-(Pivaloylamino)-7-phenyl-3,4,6,7-tetrahydrofuro[3′,2′:5,6]pyrido[2,3-*d*]pyrimidin-4-one (8c): carried out in bromobenzene as solvent for 14 h; white solid, 85% yield; mp 183–184 °C; ^1H NMR ($CDCl_3$) δ 12.00 (br s, 1 H), 8.46 (br s, 1 H), 8.25 (s, 1 H), 7.40 (m, 5 H), 5.98 (m, 1 H), 3.83–3.75 (m, 1 H), 3.36–3.28 (m, 1 H), 1.33 (s, 9 H); HRMS calcd for $C_{20}H_{20}N_4O_3$, *m/z* 364.1535, found *m/z* 364.1536.

2-(Pivaloylamino)-3,4,6,7-tetrahydro-8*H*-pyrano[3′,2′:5,6]pyrido[2,3-*d*]pyrimidin-4-one (8d): carried out in *o*-dichlorobenzene as solvent for 2 weeks; pale yellow crystals, 55% yield; mp 256–258 °C dec, ^1H NMR ($CDCl_3$) δ 11.94 (br s, 1 H), 8.40 (br s, 1 H), 8.18 (s, 1 H), 4.47 (t, J = 5.2 Hz, 2 H), 2.92 (t, J = 6.4 Hz, 2 H), 2.12–2.04 (m, 2 H), 1.33 (s, 9 H); HRMS calcd for $C_{15}H_{18}N_4O_3$, *m/z* 302.1379, found *m/z* 302.1365.

2-(Pivaloylamino)-3,4,6,7-tetrahydropyrrolo[3′,2′:5,6]pyrido[2,3-*d*]pyrimidin-4-one (8e): carried out in *o*-dichlorobenzene as solvent for 92.5 h, tan solid (after purification by preparative TLC using 1:1 acetonitrile/methylene chloride as eluent), 3% yield; mp 214–219 °C dec; ^1H NMR ($CDCl_3$) δ 12.08 (br s, 1 H), 8.18 (br s, 1 H), 8.15 (s, 1 H), 4.19 (t, J = 8.2 Hz, 2 H), 3.10 (t, J = 8.3 Hz, 2 H), 1.86 (br s, 1 H), 1.35 (s, 9 H); HRMS calcd for $C_{14}H_{17}N_5O_2$, *m/z* 287.1382, found *m/z* 287.1374.

Registry No. 1, 7271-94-5; **2a**, 111934-33-9; **2b**, 111934-34-0; **2c**, 111934-35-1; **2d**, 111934-36-2; **2e**, 111934-37-3; **3**, 111934-38-4; **4a**, 111934-39-5; **4b**, 111934-40-8; **4c**, 111934-41-9; **4d**, 111934-42-0; **4e**, 111934-43-1; **5**, 111934-44-2; **6**, 111934-45-3; **7a**, 111934-46-4; **7b**, 111934-47-5; **7c**, 111934-48-6; **7d**, 111934-49-7; **7e**, 111934-50-0; **8a**, 111934-51-1; **8b**, 111934-52-2; **8c**, 111934-53-3; **8d**, 111934-54-4; **8e**, 111934-55-5; 4-amino-1-butyne, 14044-63-4; 7-chloro-1,3-dimethyl-6-azalumazine, 54632-27-8; 4-pentyn-1-ol, 5390-04-5; 3-butyn-1-ol, 927-74-2; 5-hexyn-3-ol, 19780-84-8; α-2-propylbenzenemethanol, 1743-36-8.

Thermally Irreversible Photochromic Systems. Reversible Photocyclization of Diarylethene Derivatives

Masahiro Irie* and Masaaki Mohri

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan

Received August 3, 1987

The reversible photocyclization of 1,2-diarylethene derivatives having methyl-substituted heterocyclic rings has been found to constitute a photochromic system, which is both thermally irreversible and fatigue resistant. *cis*-1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (**3d**) undergoes a photocyclization to produce the dihydro derivative of benzodithiophene (**4d**) with λ_{max} at 512 nm, which is stable for more than 12 h at 80 °C. The colored form reverts to the cis form on exposure to visible light ($\lambda > 500$ nm). The absorption maximum of the colored form shifts to 560 nm, when the cyano residues are replaced by an acid anhydride group. Upon irradiation with 405-nm light, the acid anhydride derivative, 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**5**), cyclizes to the thermally stable dihydro form (**6**) with the quantum yield of 0.08 ± 0.01. No change in the visible absorption at 560 nm and the NMR spectrum is observed at 80 °C. Coloring and bleaching cycles can be repeated more than 100 times under deaerated conditions. Quantum yield for bleaching reaction has been found to depend on the wavelength of excitation. The quantum yield, 0.14 ± 0.02, at the excitation wavelength of 546 nm decreases to 0.04 at the wavelength of 633 nm. Both compounds do not show any thermochromic reaction even at 300 °C.

Introduction

Photochromism is defined as a reversible change in a chemical species between two forms having different absorption spectra,

$$A \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} B$$

Organic compounds that possess the photochromic property have attracted a significant amount of attention from the view point of using them as optical memory media. Hirshberg mentioned, for the first time, that the cycle of photocoloring and photobleaching constituted a chemical memory model.[1] Despite favorable conditions provided

---

(1) Hirschberg, Y. *J. Am. Chem. Soc.* **1956**, *78*, 2304.

0022-3263/88/1953-0803$01.50/0

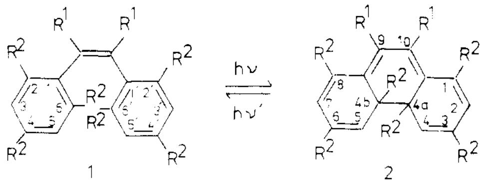
by the recent development of laser technology, organic photochromic compounds have found little application in optical information storage. Among the various reasons for this, the more important ones are the lack of thermal stability of the colored form and the low fatigue resistance of the compounds, both thermal and photochemical.

A feasible way to resolve the deficiencies is to find out thermally stable photochromic systems and to search for fatigue-resistant compounds among them. In contrast to the vast number of studies on photochromic compounds,[2] relatively few papers have been published on thermally stable photochromic systems. (*E*)-α-(2,5-Dimethyl-3-furylethylidene)-β-isopropylidenesuccinic anhydride (furyl fulgide) synthesized by Heller is one of such photochromic compounds.[3-8] One undesirable property of the furyl fulgide for optical data recording is that the compound has a thermochromic behavior at elevated temperature. The colorless form turned to red above 120 °C.

In the present paper, we report on a new type of thermally stable photochromic system, arylethene derivatives. The compounds have no thermochromic property and the colored form is stable even at elevated temperature.

Results

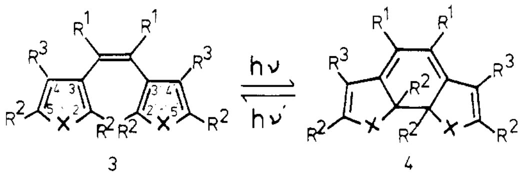
1. **2,3-Dimesityl-2-butene.** Trans–cis isomerization of stilbene is a well-known photochemical reaction, which has been most extensively studied.[9] In addition to the trans–cis isomerization, stilbene-like molecules undergo a reversible cyclization reaction upon ultraviolet irradiation.[10] This is a variation of ring closure of 1,3,5-hexatriene to 1,3-cyclohexadiene. When R^2 is hydrogen, the photogenerated dihydrophenanthrene further converts to 9,10-disubstituted phenanthrene by the reaction with oxygen.



1 2

cis-2,3-Dimesityl-2-butene (**1**, $R^1 = R^2 = CH_3$) was synthesized and the photochemical reaction was followed by absorption measurement in the presence of oxygen. Upon ultraviolet irradiation (λ 289 nm), a yellow color appeared at 445 nm. According to the assignment of Muszkat and Fischer,[10] the absorption is attributable to the dihydro derivative of the 9,10-dimethylphenanthrene (**2**, $R^1 = R^2 = CH_3$). In the dark, the yellow color disappeared in 3 min at 30 °C. 9,10-Dimethylphenanthrene ring formation was not discerned in the spectrum in contrast with stilbene having hydrogens at R^2 positions. The methyl groups at the 4a and 4b positions in the dihydrophenanthrene ring are stable enough not to be split off from the the ring by oxygen. Although the introduction of methyl substituents at the 2 (or 6) and 2′ (or 6′) positions of the phenyl rings of **1** prevents the irreversible oxidation reaction, the photogenerated dihydro form is unstable and reverts quickly to the open-ring form. Compound **2** cannot meet the the thermal stability requirement.

2. **2,3-Di(3-furyl)-2-butene and 2,3-Di(3-thienyl)-2-butene.** With the aim of prolonging the lifetime of the dihydro form, we replaced the phenyl groups of **1** by heterocyclic groups. Kellogg et al.[11] studied a new synthetic route to condensed ring systems including heteroatoms from 1,2-diarylethene derivatives having heterocyclic groups. Photolysis of the difuryl- and dithienylethene derivatives results in ring closure to form dihydro intermediates. The intermediates lose hydrogen by oxidation to form the condensed ring with heteroatoms. In the paper, they mentioned that the dihydro intermediate (**4a**, X = S, $R^1 = R^2 = R^3 = H$) of 1,2-di(3-thienyl)ethene is stable for periods of 12–15 h in the dark in the absence of oxygen.



3 4

3a, X = S; $R^1 = R^2 = R^3 = H$
3b, X = S; $R^1 = R^2 = CH_3$; $R^3 = H$
3c, X = O; $R^1 = R^2 = CH_3$; $R^3 = H$
3d, X = S; $R^1 = CN$; $R^2 = R^3 = CH_3$

4a, X = S; $R^1 = R^2 = R^3 = H$
4b, X = S; $R^1 = R^2 = CH_3$; $R^3 = H$
4c, X = O; $R^1 = R^2 = CH_3$; $R^3 = H$
4d, X = S; $R^1 = CN$; $R^2 = R^3 = CH_3$

The lifetime is much longer than that of the dihydro intermediate of stilbene derivatives, such as **1**. This result suggests that the substitution of heterocyclic groups for the phenyl groups will prolong the lifetime of the dihydro form. We synthesized 2,3-bis(2,5-dimethyl-3-thienyl)-2-butene (**3b**, X = S, $R^1 = R^2 = CH_3$, $R^3 = H$) and 2,3-bis(2,5-dimethyl-3-furyl)-2-butene (**3c**, X = O, $R^1 = R^2 = CH_3$, $R^3 = H$) having methyl groups at R^1 and R^2 positions and studied the photochemistry hoping to find a photochromic system that would show a resistance to oxidation and have thermal stability.

Compound **3b** was prepared by the coupling reaction of two 2,5-dimethyl-3-acetylthiophenes. The butene thus obtained was a mixture of the trans and cis forms. The cis form was isolated by column chromatography and used for the following experiments. Compound **3c** was prepared by a similar method from 2,5-dimethyl-3-acetylfuran.

Ultraviolet irradiation (λ 313 nm) of degassed benzene solutions of **3b** and **3c** led to the formation of yellow color. The absorption maxima were observed at 431 nm for **4b** and at 391 nm for **4c**. Exposure of the solutions to visible light (λ >390 nm) led to rapid disappearance of the yellow color. The color could be regenerated by irradiation with 313-nm light. The yellow color is attributable to the ring-closed form (**4**, X = O, S, $R^1 = R^2 = CH_3$, $R^3 = H$). Exposure to the air caused no decrease of the yellow color. Oxygen did not convert the dihydro form into the condensed ring. After several cycles, only a small part of the compounds was found to convert to the trans form, which was detected by liquid chromatography.

The photogenerated ring-closed forms (**4b** and **4c**) were very stable even at elevated temperature. The absorption

---

(2) Brown, G. H., Ed. *Photochromism*; Wiley-Interscience: New York, 1971.

(3) Heller, H. G. *Chem. Ind.* (*London*) 1978, 193.

(4) Heller, H. G.; Oliver, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 197.

(5) Darcy, P. J.; Heller, H. G.; Strydom, P. J.; Whittall, J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 202.

(6) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 341.

(7) Glaze, A. P.; Harris, S. A.; Heller, H. G.; Johncock, W.; Oliver, S. N.; Strydom, P. J.; Whittall, J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 957.

(8) Heller, H. G. *Proc. IEEE* **1983**, *130*, 209.

(9) Saltiel, J.; D Agostino, J.; Megarity, E. D.; Metts, J.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.

(10) Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1967**, 662.

(11) Kellogg, R. M.; Groen, M. B.; Wynberg, H. *J. Org. Chem.* **1967**, *32*, 3093.

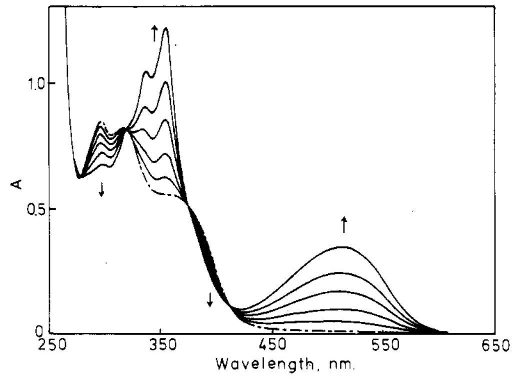


Figure 1. Absorption spectral change of CCl_4 solution of **3d** (1×10^{-4} M) (---) by irradiation with 405-nm light.

spectra remained constant for more than 12 h at 80 °C. The long lifetime is due to the absence of an oxidation reaction. The introduction of methyl groups at the 2 and 5 positions of the thiophene and furan rings prevents the oxidation reaction to produce condensed rings. The methyl groups are not eliminated from the dihydro forms (**4b** and **4c**) by oxygen in contrast to hydrogens. The thermal stability of the dihydro forms having heteroatoms suggests that the photocyclization reaction is a promising photochromic system for optical data storage media. The absorption bands of the compounds **4b** and **4c** lie, however, in the wavelength range shorter than 500 nm and the reaction of the compounds cannot be efficiently induced by conventional laser lights such as Ar ion laser (λ 488, 514 nm) or He–Ne laser (λ 633 nm). In addition, the side reaction to produce the trans form limits the number of possible coloration and bleaching cycles. In order to shift the absorption maximum to longer wavelength, we synthesized cyano and acid anhydride derivatives.

3. 1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene. The cyano derivative (**3d**, X = S, R^1 = CN, R^2 = R^3 = CH_3) was prepared by the coupling reaction of two 2,4,5-trimethyl-3-(cyanomethyl)thiophenes. The mixed products of the trans and cis form were dissolved in acetonitrile and exposed to ultraviolet light (λ >350 nm). The irradiation converted the trans form to the cis form and led to the precipitation of the less soluble cis form, which was separated from the solution by filtration and purified by recrystallization from a hexane–ether mixture. This material was used for further experiments.

Figure 1 shows the absorption spectral change of CCl_4 solution of **3d** by photoirradiation with 405-nm light. Irradiation of the CCl_4 solution with 405-nm light led to the decrease of the absorption at 297 nm and the formation of a red solution, in which a visible absorption at 512 nm was observed. The introduction of cyano groups shifted the absorption maximum to a longer wavelength by as much as 81 nm. Isosbestic points were observed at 277, 320, 377, and 410 nm. Any indication of the formation of the trans form was not discerned from the absorption spectrum. Upon visible irradiation (λ >500 nm) the red color disappeared along with the ultraviolet absorption at 355 nm and the initial cis form absorption was restored.

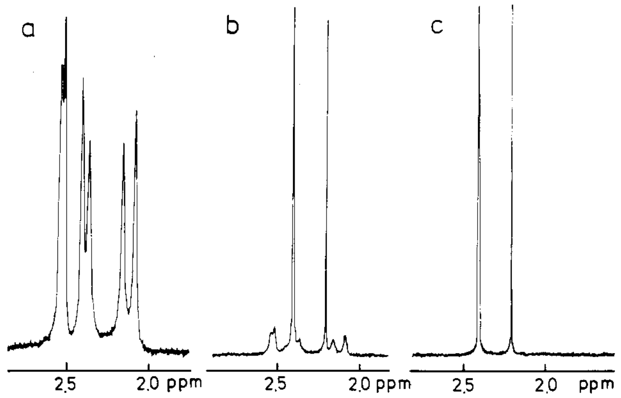


Figure 2. NMR Spectra (360 MHz) of **3d** in CCl_4: (a) before irradiation; (b) in the photostationary state under irradiation with 405-nm light; (c) (b) − 0.4(a).

Figures 2a and 2b show the 360-MHz NMR spectra of methyl protons of **3d** in CCl_4 before photoirradiation and in the photostationary state under irradiation with 405-nm light, respectively. Subtraction of the remaining methyl protons of the cis form from the spectrum b yielded the spectrum c. The absence of other signals except the two lines at 2.22 and 2.41 ppm due to the dihydro form also indicates that the cis to trans isomerization is negligible when the sample is irradiated with light of wavelength 405 nm. The six lines observed before photoirradiation indicate the existence of two conformations in the compound **3d**. One conformer has two thiophene rings in mirror symmetry and the other C_2 symmetry. The broadening of the six methyl signals is explained by the interconversion of the two conformers, which is induced by the rotation of the thiophene rings. The broadness of 2.41-ppm signal after photoirradiation arises from the near equivalence in chemical shift of two different kinds of methyl groups. The conversion of the cis form to the dihydro form in the photostationary state was obtained to be 60% from the spectrum b.

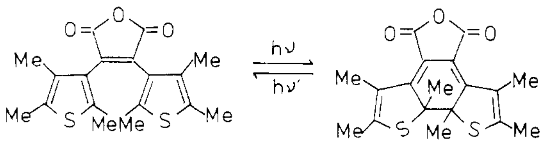
The photogenerated ring-closed form was stable even at elevated temperature. The absorption spectrum at 512 nm as well as the NMR signals at 2.22 and 2.41 ppm due to the dihydro form remained constant for more than 12 h at 80 °C. Any reversion from the ring-closed form to the cis form was not discerned from the NMR spectrum after the solution containing the dihydro form was kept at 80 °C for 12 h. In addition, the cis form did not show any thermal coloration reaction, thermochromism, even at 300 °C. The absence of thermochromic reaction suggests that the disrotatory ring closure reaction is prohibited because the ring-closure requires the loss of aromatic character of two thiophene rings and also R^2 bulky methyl groups in the cis position of the ring-closed form cause steric repulsive force.

Although the introduction of cyano groups shifted the absorption band of the dihydro form to longer wavelength, the band is still shorter than 600 nm. In order to shift the absorption band further to longer wavelength and to prohibit the cis to trans isomerization completely, the cyano groups were converted to an acid anhydride group.

4. 2,3-Bis(2,4,5-trimethyl-3-thienyl)maleic Anhydride. The acid anhydride derivative **5** was prepared by hydrolysis of **3d** with KOH in ethylene glycol monoethyl ether–water mixture. Compound **5** is soluble in nonpolar solvents such as benzene or CCl_4.

Figure 3 shows the absorption spectra of **5** in benzene before photoirradiation and in the photostationary state under irradiation with 405-nm light. Upon irradiation with 405-nm light, the solution became brown and a new absorption peak appeared at 560 nm. The absorption maximum shifts to longer wavelength by 48 nm in comparison with the dicyano derivative **4d**. The new band is ascribable to the ring-closed dihydro form **6**. Upon exposure of the brown solution to the visible light (λ >520 nm), the solution again became yellow and the initial absorption was restored.

Figure 4 shows the NMR spectra of methyl protons of **5** in CCl_4. Before photoirradiation, six lines were observed



5 6

that are due to the existence of two conformers as described in the case of **3d**. Upon irradiation with 405-nm light, three new lines appeared at 2.28, 2.42, and 2.49 ppm along with a decrease of the intensity of the six lines. Subtraction of the six lines from the spectrum b yielded the spectrum c. The three lines are assigned to the methyl protons of the closed-ring form. No side reaction was detected from the NMR spectra. The conversion of the open-ring to dihydro form in the photostationary state under irradiation with 405-nm light was obtained to be 60% from the spectrum b.

The photogenerated dihydro form was very stable. Any changes of the absorption intensity at 560 nm and the intensity ratio of the three lines to the six lines in the NMR spectrum was not observed at 80 °C. The thermal stability of the dihydro forms of **2**, **4b**, **4c**, **4d**, and **6** were compared under the same conditions in toluene at 80 °C. Except **2**, which disappeared in 3 min at 30 °C, the compounds having heteroatoms in the dihydro form, **4b**, **4c**, **4d**, and **6**, keep the absorption intensity constant for more than 12 h at 80 °C. The difference in the thermal stability between the compound **2** and the compounds having heteroatoms may be ascribed to the difference in the aromatic stabilization energy of the phenyl and heterocyclic rings gained in the ring-opening process.

The acid anhydride derivative **5** also did not show any thermochromic reaction. It melts at 161.5 °C without changing the initial yellow color. The yellow color remained even when the temperature was increased to 300 °C.

It is difficult to compare quantitatively the fatigue resistance, i.e., how many times coloration and decoloration cycles can be repeated without permanent product formation, because the property strongly depends on the environmental conditions, such as the solvent or matrix. We tried to measure qualitatively the fatigue of **3b**, **3c**, **3d**, and **5** in benzene in the presence and absence of air, as shown in Table I. Furyl fulgide was also measured under the same conditions. The repeatable cycle number indicates the cycle number when the colored intensity decreases to 80% of the first cycle. The acid anhydride derivative showed the best fatigue resistance, which is superior to that of furyl fulgide under the present conditions. Elimination of oxygen from the solution increases the cycle number.

The absorption tail of the dihydro form of **6** reaches 700 nm and He–Ne laser can bleach the colored form. This indicates that the chromophore may find applications for optical data storage media. Further study to shift the band to longer wavelength by more than 100 nm, is, however, necessary to provide photosensitivity to the diode laser light (780 to 830 nm).

The quantum yields of coloration and decoloration reactions were measured in benzene and CCl_4. Mercury lines, which were isolated with a monochromator, were used to induce the reactions. Table II summarizes the results. The coloration quantum yield was around 0.1. A slight increase of the quantum yield with shorter wavelength excitation was observed. The decoloration quantum yield strongly depends on the wavelength of excitation. The quantum yield with 633-nm light is around $^1/_4$ of that with 546-nm light. Figure 5 shows the relation of the quantum yield on the wavelength of excitation. The relation suggests that the quantum yield becomes zero at the absorption edge of 680 nm.

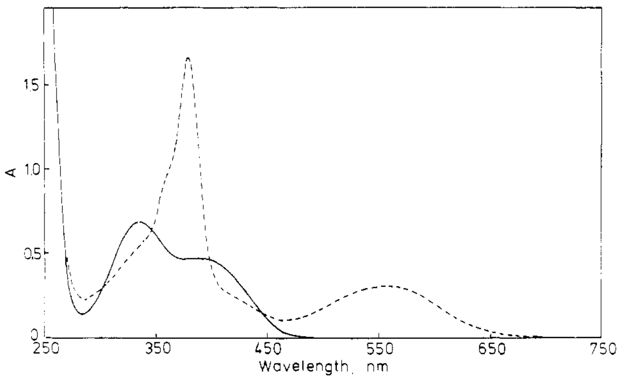


Figure 3. Absorption spectra of **5** (1×10^{-4}) (—) and in the photostationary state under irradiation with 405-nm light (---).

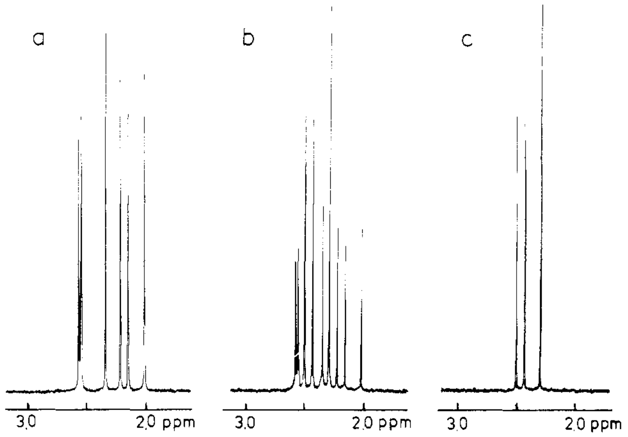


Figure 4. NMR spectra (360 MHz) of **5** in CCl_4: (a) Before irradiation; (b) in the photostationary state under irradiation with 405-nm light; (c) (b) − 0.4(a).

Table I. Fatigue-Resistant Propery of Diarylethene Derivatives[a]

compd	irradiation wavelength, nm: coloring	irradiation wavelength, nm: bleaching	repeatable cycle no.[b]
3b	313	435	3
3c	313	405	3
3d	405	546	10
5	405	546	70
5[c]	405	546	>100
furyl fulgide	366	546	21

[a] Irradiation was carried out in the presence of air. Concentration of the compounds is 1×10^{-4} M in benzene. Photostationary state can be reached by 5-min irradiation. [b] The cycle number when the colored intensity decreased to 80% of the first cycle. [c] In the absence of air.

Table II. Quantum Yields for Coloring of 5 and Bleaching of 6

	excitation wavelength, nm	solvent: CCl_4	solvent: benzene
5 → **6**	366	0.11	*a*
	405	0.09	0.07
6 → **5**	546	0.15	0.12
	577	0.09	0.07
	633	0.04	*a*

[a] Not measured.

The anomalous wavelength dependence of the quantum yield has been observed in several systems.[12-17] The

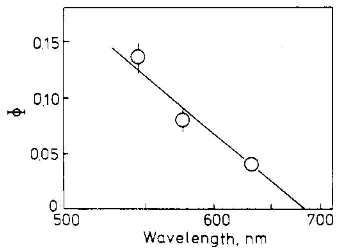


Figure 5. Relation of the quantum yield for bleaching of **6** on the wavelength of excitation.

quantum yield of photoisomerization of hexafluorobenzene to its "Dewar" isomer in the gas phase is reported to increase with an increase in the photon energy.[12] The vibrationally "hot" state is believed to be responsible for the abnormal behavior. Similar wavelength dependence of the quantum yield is reported in solution for the isomerization of fulgide derivatives.[13-15] The wavelength dependence was interpreted by considering vibronic effects.

One of the interpretations of the present wavelength dependence is the vibronic mechanism. Excess vibronic energy is necessary to induce the ring-opening reaction. The very low quantum yield at the absorption tail, where excess vibrational energy is very small, supports the mechanism. The mechanism, however, is inconsistent with the fact that vibrational relaxation in solution is usually very fast and chemical reaction can rarely compete with the relaxation process. Another interpretation is to postulate the superposition of two bands of different electronic nature in the broad absorption band from 480 to 700 nm, the band in the shorter wavelength being responsible for the ring-opening reaction. The existence of the two conformations, one of which has a shorter wavelength band and is responsible for the ring-opening reaction, can also explain the anomalous wavelength dependence. At the present moment, we have no definite evidence for which mechanism operates in the present system.

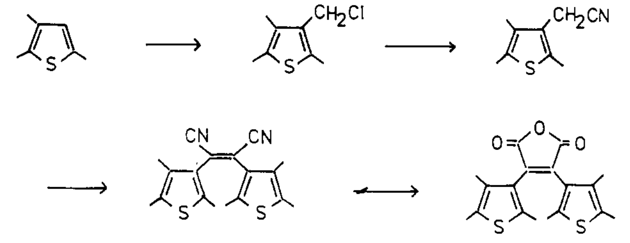
Experimental Section

Materials. 2,3-Dimesityl-2-butene (1).[18] 2,4,6-Trimethylacetophenone (32 g, 0.20 mol) was added to the suspension of zinc powder (52 g, 0.80 mol) in 300 mL of THF at −10 °C under nitrogen. Then $TiCl_4$ (76 g, 0.40 mol) was added slowly with vigorous stirring. After the reaction mixture was stirred for 2 h below 0 °C, the solution was refluxed for 8 h. The reaction mixture was poured into 10% potassium carbonate solution and then the product was extracted with ether. Compound **1** was isolated in 40% yield by column chromatography on silica: ^1H NMR ($CDCl_3$) δ 1.57 (s, 6 H, $=CCH_3$), 2.20, 2.27, 2.40, 2.53 (18 h, $ArCH_3$), 6.80 (m, 4 H, Ar H); mass spectrum, *m/e* M^+ 292, $M^+ - CH_3$ 277.

2,3-Bis(2,5-dimethyl-3-thienyl)-2-butene (3b).[18] $TiCl_4$ (28 g, 0.15 mol) was added slowly to the suspension of zinc powder (20 g, 0.30 mol) in 400 mL of THF at −10 °C under nitrogen. Then 2,5-dimethyl-3-acetylthiophene[19] (16 g, 0.10 mol) in 200 mL of THF was added dropwise. After the reaction mixture was stirred for 2 h at room temperature, followed by alkaline hydrolysis with 10% potassium carbonate solution and ether extraction, **3b** was obtained in 20% yield by column chromatography on silica gel. The crude product was purified by recrystallization from a hexane–ether mixture: ^1H NMR ($CDCl_3$) δ 1.90 (s, 6 H, $=CCH_3$), 2.00 (s, 6 H, $ArCH_3$), 2.27 (s, 6 H, $ArCH_3$), 6.07 (s, 2 H, Ar H); mass spectrum, *m/e* M^+ 276, $M^+ - CH_3$ 261.

2,3-Bis(2,5-dimethyl-3-furyl)-2-butene (3c). The synthetic procedure was the same as for **3b**. 2,5-Dimethyl-3-acetylfuran was used instead of 2,5-dimethyl-3-acetylthiophene: ^1H NMR ($CDCl_3$) δ 1.83 (s, 6 H, $=CCH_3$), 1.97 (s, 6 H, $ArCH_3$), 2.17 (s, 6 H, $ArCH_3$), δ 5.63 (s, 2 H, Ar H); mass spectrum, *m/e* M^+ 244, $M^+ - CH_3$ 229.

1,2-Bis(2,3,5-trimethyl-3-thienyl)maleic anhydride was synthesized from 2,3,5-trimethylthiophene[20] as follows.



2,3,5-Trimethyl-4-(chloromethyl)thiophene. Chloromethyl methyl ether (97 g, 1.2 mol) was added dropwise to a solution of 2,3,5-trimethylthiophene (90 g, 0.70 mol) in 300 mL of CS_2 at 0 °C. To this solution was added, over a period of 1 h, $SnCl_4$ (52 g, 0.20 mol), and then the solution was stirred for 1 h. The reaction mixture was poured on ice and the organic layer was separated and dried over calcium chloride. Removal of the solvent and distillation of the residue under vacuum gave 2,3,5-trimethyl-4-(chloromethyl)thiophene in 50% yield: bp 58 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 2.07 (s, 3 H, $ArCH_3$), 2.23 (s, 3 H, $ArCH_3$), 2.33 (s, 3 H, $ArCH_3$), 4.40 (s, 2 H, $ArCH_2Cl$).

2,3,5-Trimethyl-4-(cyanomethyl)thiophene. NaCN (28 g, 0.48 mol) and triethylbenzylammonium chloride (1 g, 0.0048 mol) was dissolved in 50 mL of water at 30 °C. To this solution was added 2,3,5-trimethyl-4-(chloromethyl)thiophene (57 g, 0.32 mol), and the solution was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was poured into water and then the product was extracted with ether. Removal of the ether and distillation of the oily product under vacuum gave 2,3,5-trimethyl-4-(cyanomethyl)thiophene in 85% yield: bp 78 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 2.07 (s, 3 H, $ArCH_3$), 2.27 (s, 3 H, $ArCH_3$), 2.33 (s, 3 H, $ArCH_3$), 3.43 (s, 3 H, $ArCH_2CN$).

1,2-Dicyano-1,2-bis(2,3,5-trimethyl-3-thienyl)ethene (3d). To 20 mL of 50% NaOH aqueous solution containing triethylbenzylammonium chloride (0.21 g, 0.0010 mol) was added a mixture of 2,3,5-trimethyl-4-(cyanomethyl)thiophene (16 g, 0.10 mol) and CCl_4 (15 g, 0.10 mol) at 40 °C. The solution was stirred for 1.5 h at 45 °C. The reaction mixture was poured into water and the product was extracted with ether and chloroform. After the solvent was removed, the mixture of trans and cis forms (**3d**) was isolated in 47% yield by column chlomatography on silica gel. The mixed product was dissolved in acetonitrile and then exposed to ultraviolet light (λ >350 nm). The cis form precipitated was separated from the solution by filtration and then purified by recrystallization from a hexane–ether mixture: mp 164 °C; ^1H NMR ($CDCl_3$) δ 2.10, 2.17, 2.36, 2.41, 2.53, 2.54 (6 H, $ArCH_3$); mass spectrum, *m/e* M^+ 326, $M^+ - CH_3$ 311. Anal. Calcd for $C_{18}H_{18}N_2S_2$: C, 66.26; H, 5.52; N, 8.59. Found: C, 66.26; H, 5.38; N, 8.56.

2,3-Bis(2,3,5-trimethyl-3-thienyl)maleic Anhydride (5). Compound **3d** (6 mmol) and ethylene glycol monoethyl ether (5 mL) were added to 5 mL of a 50% potassium hydroxide aqueous solution, and the solution was refluxed for 24 h. The reaction mixture was poured into water and 20% hydrochloric acid aqueous solution was added until the mixture became acidic. The yellow precipitate was extracted with ether. After the ether was removed, **5** was isolated in 20% yield by column chromatography on silica gel. The crude product was purified by recrystallization from a ether–hexane mixture: mp 161.5 °C; ^1H NMR ($CDCl_3$) δ 2.01, 2.14, 2.21, 2.34, 2.54, 2.56 (6 H, $ArCH_3$); mass spectrum, *m/e* M^+ 346, $M^+ - CH_3$ 331. Anal. Calcd for $C_{18}H_{18}O_3S_2$: C, 62.40; H, 5.24; S, 18.51. Found: C, 62.68; H, 5.18; S, 18.48.

Photoisomerization. A mercury lamp (Ushio, 1 kW) was used as a light source. Mercury lines, 335, 366, 405, 546, and 577 nm,

---

[12] Haller, I. *J. Chem. Phys.* **1967**, *47*, 1117.

[13] Santiago, A.; Becker, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 3654.

[14] Becker, R. S.; Dolan, E.; Balke, D. E. *J. Chem. Phys.* **1969**, *49*, 239.

[15] Lenoble, C.; Becker, R. S. *J. Phys. Chem.* **1986**, *90*, 2651.

[16] Moradpour, A.; Nicoud, J. F.; Balavoine, G.; Kagan, H; Tsoucaris, G. *J. Am. Chem. Soc.* **1971**, *93*, 2353.

[17] Bernstein, W. J.; Calvin, M.; Buchardt, O. *J. Am. Chem. Soc.* **1972**, *94*, 494.

[18] Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041.

[19] Hartough, H. D.; Kosak, A. I. *J. Am. Chem. Soc.* **1947**, *69*, 3098.

[20] Youtz, M. A.; Perkins, P. P. *J. Am. Chem. Soc.* **1929**, *51*, 3511.

808 *J. Org. Chem.* **1988**, *53*, 808–810

were isolated by passing the light through a monochromater (Ritsu, MC-10N). A He–Ne laser was used for the light of 633 nm.

Quantum yields were determined by measuring the rate of isomerization in the initial stage of the reaction at low concentration (absorbance at the measuring wavelength < 0.2) and the light intensity was measured with a ferrioxalate actinometer and a photometer (International Light, IL 700).

Absorption spectra were measured with a spectrophotometer (Shimadzu MPS-2000) and NMR measurements were carried out with a 360-MHz NMR spectrometer (Brucker WN-360).

Registry No. 1 ($R^1 = R^2 = CH_3$), 81667-52-9; **3b**, 112440-44-5; *trans*-**3b**, 112459-53-7; **3c**, 112440-45-6; **3d**, 112440-46-7; *trans*-**3d**, 112440-50-3; **4d**, 112440-51-4; **5**, 112440-47-8; **6**, 112440-48-9; furyl fulgide, 77515-04-9; 2,3,5-trimethyl-4-(chloromethyl)thiophene, 63826-43-7; 2,3,5-trimethyl-4-(cyanomethyl)thiophene, 112440-49-0; 2,4,6-trimethylacetophenone, 1667-01-2; 2,5-dimethyl-3-acetylthiophene, 2530-10-1; 2,5-dimethyl-3-acetylfuran, 10599-70-9; 2,3,5-trimethylthiophene, 1795-05-7.

Oxidation of Cyclic Ketones Catalyzed by Polyethylene Glycol and Rhenium Carbonyl under Basic and Exceptionally Mild Conditions

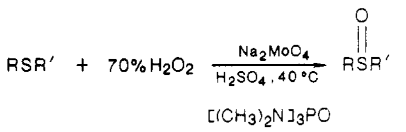
Krystyna Osowska-Pacewicka and Howard Alper*[1]

Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Received July 31, 1987

Monocyclic ketones react with oxygen, potassium hydroxide, potassium carbonate, and catalytic amounts of rhenium carbonyl and polyethylene glycol (PEG-400 or $R_4N^+X^-$ or TDA-1), at room temperature and 1 atm, to give diacids in fine yields. Bicyclic ketones afford keto diacids or hydroxyquinones, depending on the nature of the substrate.

Phase-transfer catalysis is of genuine use for promoting metal-catalyzed oxidation reactions. For example, trioctylmethylammonium tungstate complexed by appropriate, lipophilic, neutral or anionic ligands catalyzes the epoxidation of olefins by hydrogen peroxide.[2] The oxidation of sulfides to sulfoxides can also occur by using tungstates or molybdates as catalysts (eq 1).[3] Oxygen can be employed as an oxidant under phase-transfer conditions. Palladium chloride catalyzed oxidation of terminal olefins to ketones (Wacker reaction) proceeds in good yields when a quaternary ammonium salt, containing at least one long-chain alkyl group, is used as the phase-transfer agent.[4] Both terminal and internal olefins can be oxidized by using either β-cyclodextrin[5] or polyethylene glycol of molecular weight 400 (eq 2).[6]



$$RSR' + 70\%\,H_2O_2 \xrightarrow[H_2SO_4,\ 40\,°C]{Na_2MoO_4} RS(=O)R' \qquad [(CH_3)_2N]_3PO$$

(1)

$$RCH{=}CH_2 + O_2 \xrightarrow[\text{PEG-400, } H_2O \text{; } 65\ °C,\ 1\ \text{atm}]{PdCl_2,\ CuCl_2{\cdot}2H_2O} RCOCH_3 \qquad (2)$$

The conversion of cyclic ketones to diacids is another process of considerable industrial value.[7] It has been reported that rhenium carbonyl can catalyze the oxidation of cyclohexanone, cyclopentanone, and cycloheptanone to diacids by means of molecular oxygen.[8] However, elevated temperatures (96–98 °C) and pressures (300–500 psi) are required, and product yields are not high. A second method of autoxidation of ketones involves the use of sodium or potassium hydroxide, or alkoxides, in hexamethylphosphoramide at 23.5 or 80 °C.[9] Only moderate yields of diacids resulted for cyclic systems larger than cyclohexanone. We now report that, by the use of catalytic quantities of polyethylene glycol and rhenium carbonyl in basic media, one can achieve the oxidation of cyclic ketones in fine yields, and under exceptionally mild conditions.

Treatment of cyclohexanone with oxygen, potassium hydroxide, potassium carbonate, and catalytic quantities of rhenium carbonyl and PEG-400, in 1,2-dimethoxyethane (DME) for 24 h at room temperature and 1 atm, afforded pure adipic acid in 74% yield. The ratio of cyclohexanone to $Re_2(CO)_{10}$ was 100:1. As the results in Table I indicate, low product yields are attained in the absence of either the phase-transfer agent, the metal catalyst, and one or both potassium bases. Sodium carbonate and sodium hydroxide are inferior to their potassium analogues as is the use of hexane or methylene chloride as the organic solvent. Note that tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1)[10] and quaternary ammonium salts (e.g., benzyltriethylammonium chloride) are also useful phase-transfer agents for the oxidation reaction. Rhenium trichloride is ineffective as a catalyst for the oxidation reaction.

A series of monocyclic ketones (eq 3) were subjected to rhenium carbonyl catalyzed oxidation in the presence of

---

[1] Killam Research Fellow, 1986–1988.

[2] Quenard, M.; Bonmarin, V.; Gelbard, G. *Tetrahedron Lett.* **1987**, *28*, 2237 and references cited therein.

[3] Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. *J. Org. Chem.* **1985**, *50*, 2688.

[4] Januszkiewicz, K.; Alper, H. *Tetrahedron Lett.* **1983**, *24*, 5159.

[5] Zahalka, H. A.; Januszkiewicz, K.; Alper, H. *J. Mol. Catal.* **1986**, *35*, 249.

[6] Alper, H.; Januszkiewicz, K.; Smith, D. J. H. *Tetrahedron Lett.* **1985**, *26*, 2263.

[7] Luedecke, V. D. In *Encyclopedia of Chemical Processing and Design*; McKetta, J. J., Cunningham, W. A., Eds.; Dekker: New York, 1977; Vol. 2, pp 128–146.

[8] Roundhill, D. M.; Dickson, M. K.; Dixit, N. S.; Sudha-Dixit, B. P. *J. Am. Chem. Soc.* **1980**, *102*, 5538.

[9] Wallace, T. J.; Pobiner, H.; Schriesheim, A. *J. Org. Chem.* **1965**, *30*, 3768.

[10] Soula, G. *J. Org. Chem.* **1985**, *50*, 3717.

0022-3263/88/1953-0808$01.50/0 © 1988 American Chemical Society