

Studies on piezochromic photochromic (*E*)-5-dicyanomethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-diphenylmethylenetetrahydrofuran-2-one and related photochromic compounds

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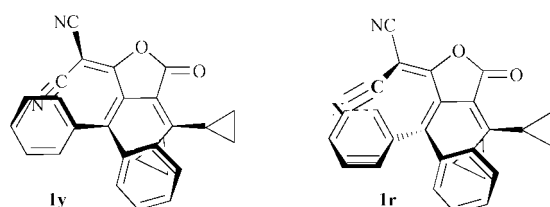
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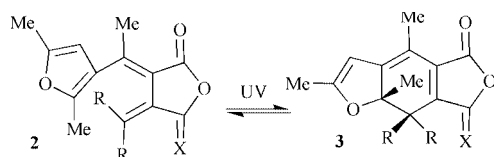
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Yellow crystals of the title compound **2b** gave a dark red powder on mechanical grinding. The yellow and red solids turned deep blue on irradiation (366 nm) and the red and blue solids turned yellow on exposure to white light. The yellow crystals gave a deep red solution in toluene, which turned blue on irradiation with ultraviolet light. The blue solution reverted to red on exposure to white light. The chemistry of these colour changes is discussed. Related photochromic compounds **2a**, **2c**, **2d**, **4a**, **4b**, **7a** and **7**, with a lesser degree of molecular overcrowding, are not piezochromic. The related non photochromic compound **1**, with the greatest degree of overcrowding, is tribochromic.

We introduced the term 'tribochromism' to describe the new phenomenon of metastable crystals that undergo a major and irreversible colour change on mechanical grinding. The coloured form is stable and does not undergo the reverse change when kept in the dark, on heating or when dissolved in an organic solvent. The phenomenon was illustrated by crystals of the folded yellow dicyanomethylene compound **1y**, which gave the deep red twisted form **1r** on mechanical grinding.¹ Piezochromic compounds undergo reversible colour changes.²



We have reported on the photochromic properties of 5-dicyanomethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-isopropylidenetetrahydrofuran-2-one **2d** which, on photocyclisation, gave blue photochrome **3d** (λ_{\max} 610 nm) showing a major bathochromic shift compared to photochrome **3c** (λ_{\max} 496 nm) from photocyclisation of the corresponding fulgide † **2c** (Scheme 1).³



a R = Ph, X = O; b R = Ph, X = C(CN)₂; c R = Me, X = O; d R = Me, X = C(CN)₂

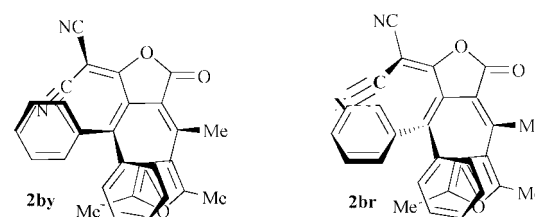
Scheme 1

Replacement of the isopropylidene group in compound **2d** by the diphenylmethylene group gave photochromic crystals of

5-dicyanomethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-diphenylmethylenetetrahydrofuran-2-one **2b** which turned out to be piezochromic and not tribochromic as expected. The difference in properties is attributed to the lesser degree of molecular overcrowding. If overcrowding is reduced further, the piezochromic properties are lost also.

Compound **2b** was prepared by the method of Moore and Khim⁴ by condensation of (*E*)-fulgide **2a** with malononitrile in the presence of diethylamine in THF, followed by cyclisation of the resulting salt with acetyl chloride.

Light-sensitive yellow crystals of compound **2b** turned blue on exposure to ultraviolet light and red on grinding. By analogy with the tribochromic compounds previously reported, the yellow form is assumed to have the folded structure **2by** and the red form to have the twisted structure **2br**. Both blue and red forms reverted to yellow on irradiation with white light.



When the yellow crystals were dissolved in toluene, a red solution (λ_{\max} 514 nm) was obtained which, on irradiation (366 nm) or boiling (110 °C), turned deep blue (λ_{\max} 610 nm). (The spectra are similar to those shown in Fig. 1.) When the blue solution was exposed to white light, it turned red. Removal of solvent and crystallisation of the residue gave yellow crystals.

The stereochemistry of compound **2b** follows from its NMR spectra, which showed a methyl group, deshielded by the carbonyl group (δ 2.44 ppm). The assignment of its structure as the 5-dicyanomethylenetetrahydrofuran-2-one derivative **2b** (and not as the 2-dicyanomethylenetetrahydrofuran-5-one derivative **8b**, Y = O) is based on the observation¹ that crystals of all eleven yellow folded tribochromic compounds and red twisted forms had adjacent diphenylmethylene and dicyanomethylene groups and gave red solutions.

† IUPAC term for fulgide is dialkylidenesuccinic anhydride.

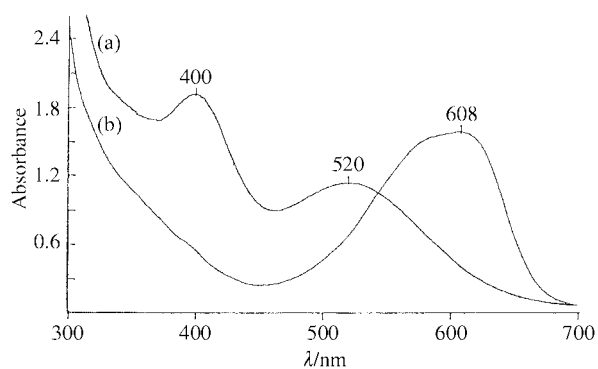
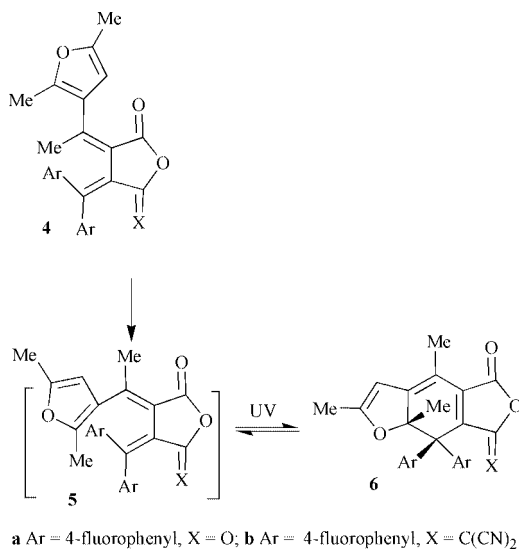


Fig. 1 The UV-Vis spectra of (*Z*)-lactone **4b** (1×10^{-4} molar solution in toluene) (a) before and (b) after heating at 110 °C.

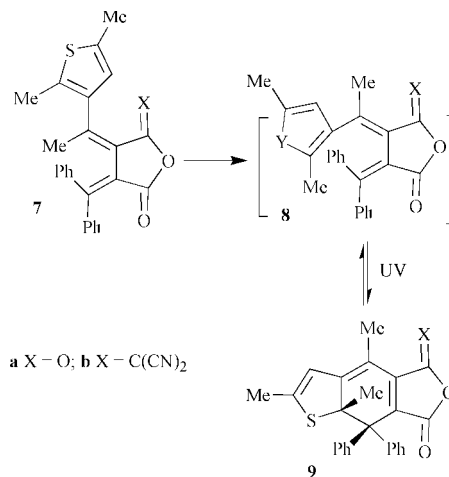
Blue photochrome, 2,4,8a-trimethyl-8,8-diphenyl-7-dicyanomethylene-5-oxo-5,7,8,8a-tetrahydrobenzo[1,2-*b*:4,5-*c*]difuran **3b** showed a characteristic high field 8a methyl signal at δ 0.90 ppm in its NMR spectrum.

(*Z*)-5-Dicyanomethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-bis(4-fluorophenyl)methylenetetrahydrofuran-2-one **4b**, red crystals, was prepared by base-catalysed condensation of the corresponding (*Z*)-fulgide **4a** with malononitrile followed by cyclisation of the resulting salt with acetyl chloride, illustrating that 5-dicyanomethylene derivatives can be obtained from either (*E*)- or (*Z*)-diarylfulgides **2a** or **4a**. The stereochemistry of (*Z*)-lactone **4b** follows from its high field methyl singlet at 1.5 ppm, due to shielding of a methyl group by the adjacent phenyl group. (*Z*)-Lactone **4b** gave a red solution in toluene (λ_{\max} 520 nm). On irradiation (366 nm) of the solution at room temperature or on boiling (110 °C), (*Z*)-lactone **4b** isomerised to the (*E*)-isomer **5b** (Scheme 2), which cyclised to the blue photochrome **6b** (λ_{\max} 608 nm) (Fig. 1).



Scheme 2

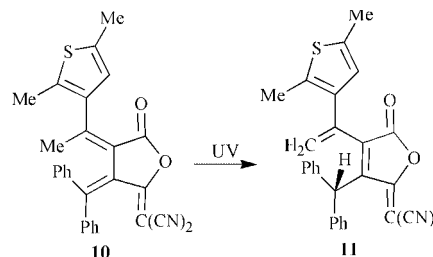
Condensation of (*Z*)-fulgide **7a** with malononitrile gave yellow crystals of (*Z*)-2-dicyanomethylene-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-diphenylmethylenetetrahydrofuran-5-one **7b** and dark red crystals of (*Z*)-5-dicyanomethylene-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-diphenylmethylenetetrahydrofuran-2-one **10**, illustrating that both 2- and 5-dicyanomethylene derivatives can be obtained in the same reaction. Their stereochemistry followed from their NMR spectra, which showed high field singlets at 1.50 and 1.44 ppm respectively due to shielding of a methyl group by a phenyl group in each case. (*Z*)-Lactones **7b** and **10** gave yellow and red solutions in toluene respectively. On irradiation (366 nm) (*Z*)-lactone **7b** in toluene (λ_{\max} 356 nm) isomerised to the (*E*)-isomer **8b**, Y = S,



Scheme 3

which cyclised to the blue photochrome **9b** (λ_{\max} 606 nm) (Scheme 3). (Photochrome **9a** shows a value of λ_{\max} 536 nm for its long wavelength absorption band.)

(*Z*)-Lactone **10**, which gave a red solution in toluene (λ_{\max} 333 and 508 nm, ϵ 6 290 and 14 300 dm³ mol⁻¹ cm⁻¹; λ_{\min} 450, ϵ 4 957 dm³ mol⁻¹ cm⁻¹), did not photoisomerise and photocyclise like (*Z*)-lactone **7b** did. On prolonged irradiation at 366 nm, it gave the maleic anhydride derivative **11** (Scheme 4), presumably by a photochemical 1,5-antarafacial H-shift. The structure of the latter was assigned from its NMR spectrum, which showed four signals at 5.42, 5.43, 6.07 and 6.13 ppm assigned to methine, two olefinic and the thienyl hydrogens, and also loss of a methyl signal.



Scheme 4

Experimental

Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. Ultraviolet and visible spectra were measured in toluene on a Cecil CE6600 spectrophotometer; infrared spectra were measured for Nujol mulls on a Perkin-Elmer 1600 FTIR spectrometer; NMR spectra were obtained with a Bruker WM360 (360 MHz) spectrometer using CDCl₃ solutions; mass spectra were recorded on a Varian Mat. CH5 spectrometer; and microanalyses were carried out using a Perkin-Elmer 240B analyser. Petrol refers to the fraction of bp 60–80 °C. Solvents were dried before use. Photocolouration (366 nm) was carried out using a 200 W medium pressure mercury lamp and an OX1A filter and photobleaching was achieved using a tungsten filament lamp.

Preparation of fulgides

First Stobbe condensation. Dimethyl succinate and ketone in toluene were added dropwise to a stirred suspension of potassium *tert*-butoxide in toluene. The mixture was stirred at room temperature (*ca.* 12 hours) and poured into water. The aqueous layer was acidified with hydrochloric acid and the liberated half-ester extracted with ether, dried and the solvent was removed.

Re-esterification. Acetyl chloride (1.5 equiv.) was added to the half-ester in methanol and the mixture boiled (6 h). Solvent was removed under reduced pressure and the residue dissolved in ether, washed with water and with sodium bicarbonate solution, dried and the solvent removed. The diester was purified by vacuum distillation.

Second Stobbe condensation. The diester from the first condensation and ketone in toluene were added dropwise to a stirred suspension of potassium *tert*-butoxide in toluene. The mixture was stirred at room temperature (6 h) and poured into water. The aqueous layer was acidified with hydrochloric acid and the liberated half-ester was extracted with ether, dried, and the solvent removed.

Hydrolysis and cyclisation. The half-ester was boiled with 10% ethanolic KOH (6 h) and the ethanol removed under reduced pressure. The residual potassium salt was dissolved in water and the diacid liberated by addition of hydrochloric acid. The diacid was dissolved in ether, dried, and the solvent removed. Diacid in dichloromethane (DCM) was stirred with acetyl chloride at room temperature (3 h). Solvent was removed and the fulgide purified by column chromatography on silica gel using DCM and petrol as eluant followed by recrystallisation.

(E)-[1-(2,5-Dimethyl-3-furyl)ethylidene]diphenylmethylenesuccinic anhydride 2a

Dimethyl diphenylmethylenesuccinate (30 g, 0.1 mol) and 2,5-dimethyl-3-acetylfuran (13.35 g, 0.1 mol) with *t*-BuOK (11.2 g, 0.1 mol) in toluene (150 cm³) gave the half-ester as a dark gum which was hydrolysed and cyclised. (*E*)-Fulgide **2a** (1.5 g, 4% yield) was obtained as orange crystals (from petrol), mp 178–180 °C; δ_{H} 1.95 (3H, s, CH₃), 1.99 (3H, s, CH₃), 2.43 (3H, s, CH₃ *cis* to C=O), 5.32 (1H, s, 4-furyl proton) and 7.10–7.44 (10H, m, aromatics).

Dimethyl diphenylmethylenesuccinate

Dimethyl succinate (60 g) and benzophenone (70 g) with *t*-BuOK (50 g) in toluene (250 cm³) gave the half-ester, which was esterified to give dimethyl diphenylmethylenesuccinate as yellow crystals (from petrol) (79.6 g, 75% yield), mp 78–80 °C.

(Z)-Bis(4-fluorophenyl)methylene[1-(2,5-dimethyl-3-furyl)ethylidene]succinic anhydride 4a

Dimethyl (*E*)-[1-(2,5-dimethyl-3-furyl)ethylidene]succinate (14 g, 0.07 mol) and 4,4'-difluorobenzophenone (15 g, 0.07 mol) with *t*-BuOK (11.2 g, 0.1 mol) in toluene (130 cm³) gave the half-ester as a dark gum which was hydrolysed and cyclised. (*Z*)-Fulgide **4a** (1.5 g, 6.7% yield) was obtained as orange crystals (from methanol), mp 200–202 °C. Found: C, 71.30; H, 4.36; M⁺ 420. C₂₅H₁₈O₄F₂ requires C, 71.44; H, 4.28%; M 420. λ_{max} 405 nm, ϵ 5495; δ_{H} 2.22 (3H, s, CH₃), 2.30 (3H, s, CH₃), 1.50 (3H, s, CH₃ *trans* to C=O), 5.88 (1H, s, 4-furyl proton) and 7.0–7.30 (8H, m, aromatics); ν_{max} /cm⁻¹ 1810 (C=O) and 1763 (C=O).

Dimethyl (E)-[1-(2,5-dimethyl-3-furyl)ethylidene]succinate

Dimethyl succinate (50 g, 0.34 mol) and 3-acetyl-2,5-dimethylfuran (47 g, 0.34 mol) with potassium *tert*-butoxide (38 g, 0.34 mol) in toluene (100 cm³) gave the half-ester which on esterification gave a black gum. Distillation at 150–170 °C at 0.4 mmHg gave pure (*E*)-diester as a yellow oil (41 g, 45% yield).

(Z)-[1-(2,5-Dimethyl-3-thienyl)ethylidene]diphenylmethylenesuccinic anhydride 7a

Dimethyl (*Z*)-[1-(2,5-dimethyl-3-thienyl)ethylidene]succinate (15 g, 0.064 mol) and benzophenone (11.6 g, 0.064 mol) with *t*-BuOK (10 g, 0.09 mol) in THF (150 cm³) gave the half-ester which was hydrolysed and cyclised. (*Z*)-Fulgide **7a** (1.5 g, 6.7%

yield) was obtained as orange crystals (from methanol), mp 196–198 °C. Found: C, 75.17; H, 5.14; M⁺ 400. C₂₅H₂₀O₃S requires C, 75.01; H, 5.00%; M 400. λ_{max} 388 nm, ϵ 9333; δ_{H} 2.37 (3H, s, CH₃), 2.39 (3H, s, CH₃), 1.43 (3H, s, CH₃ *trans* to C=O), 6.41 (1H, s, 4-thienyl proton) and 7.10–7.50 (10H, m, aromatics).

Dimethyl (Z)-[1-(2,5-dimethyl-3-thienyl)ethylidene]succinate

Dimethyl succinate (35 g, 0.24 mol) and 3-acetyl-2,5-dimethylthiophene (37 g, 0.24 mol) with *t*-BuOK (32 g, 0.28 mol) in toluene (150 cm³) gave the half-ester which on esterification gave a black oil. Distillation at 140–150 °C at 0.1 mmHg gave pure (*Z*)-diester as a yellow oil (43 g, 64% yield).

(E)-5-Dicyanomethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-diphenylmethylenetetrahydrofuran-2-one 2b

(*E*)-[1-(2,5-Dimethyl-3-furyl)ethylidene]diphenylmethylenesuccinic anhydride **2a** (1 g, 2.6 mmol) and malononitrile (0.17 g, 2.6 mmol) were added to diethylamine (0.38 g, 5.15 mmol) in THF (10 cm³) at 0 °C and the solution was stirred at room temperature (12 h). Solvent was removed and the residue dissolved in DCM (10 cm³) was treated with acetyl chloride (10 cm³). Acetyl chloride was removed under reduced pressure and the residue crystallised (from ethyl acetate and petrol 1 : 1) giving (*E*)-tetrahydrofuran-2-one **2b** as light-sensitive yellow crystals (0.2 g, 18% yield), mp 198–200 °C (dark red melt). Found: C, 77.99; H, 4.46; N, 6.5; M⁺ 432. C₂₈H₂₀O₃N₂ requires C, 77.79; H, 4.62; N, 6.47%; M 432. λ_{max} 344 nm, ϵ 12020; δ_{H} 1.90 (3H, s, CH₃), 2.06 (3H, s, CH₃), 2.40 (3H, s, CH₃ *cis* to C=O), 5.28 (1H, s, 4-furyl proton) and 6.61–7.47 (10H, m, aromatics); ν_{max} /cm⁻¹ 2224 (CN) and 1706 (C=O).

(Z)-5-Dicyanomethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-bis(4-fluorophenyl)methylenetetrahydrofuran-2-one 4b

(*Z*)-[1-(2,5-Dimethyl-3-furyl)ethylidene]diphenylmethylenesuccinic anhydride **4a** (0.71 g, 1.69 mmol) and malononitrile (0.12 g, 1.82 mmol) were added to diethylamine (0.25 g, 3.42 mmol) in THF (15 cm³) at 0 °C and the solution was stirred at room temperature (12 h). The solvent was removed and the colourless residue dissolved in DCM (10 cm³) was treated with acetyl chloride (10 cm³). Acetyl chloride and solvent were removed under reduced pressure and the residue was crystallised (from DCM and petrol) to give dark red crystals of (*Z*)-tetrahydrofuranone **4b** (0.45 g, 57% yield), mp 172–174 °C. Found: C, 69.20; H, 3.96; N, 5.96; M⁺ 468. C₂₈H₁₈F₂O₃N₂ requires C, 77.79; H, 4.62; N, 6.47%; M 468. λ_{max} 400, 520 nm, ϵ 14790 and 8913; δ_{H} 2.24 (3H, s, CH₃), 2.28 (3H, s, CH₃), 1.50 (3H, s, CH₃ *trans* to C=O), 5.90 (1H, s, 4-furyl proton) and 7.08–7.44 (8H, m, aromatics); ν_{max} /cm⁻¹ 2226 (CN) and 1710 (C=O).

(Z)-5-Dicyanomethylene-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-diphenylmethylenetetrahydrofuran-2-one 7b and (Z)-5-dicyanomethylene-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-diphenylmethylenetetrahydrofuran-2-one 10

(*Z*)-[1-(2,5-Dimethyl-3-thienyl)ethylidene]diphenylmethylenesuccinic anhydride **7a** (1.5 g, 3.75 mmol) and malononitrile (0.25 g, 3.78 mmol) were added to diethylamine (0.85 g, 11.5 mmol) in THF (10 cm³) at 0 °C and the solution was stirred at room temperature (*ca.* 12 h). The solvent was removed and the residue dissolved in DCM (10 cm³) was treated with acetyl chloride (10 cm³). Acetyl chloride and solvent were removed under reduced pressure and the residue was crystallised from chloroform and petrol (1 : 1). The first crop of yellow crystals was (*Z*)-tetrahydrofuranone **7b** (0.1 g, 6% yield), mp 180–182 °C. Found: C, 74.84; H, 4.60; N, 6.03. C₂₈H₂₀O₂N₂S requires C, 75.02; H, 4.46; N, 6.24%. λ_{max} 356 nm, ϵ 21380; δ_{H} 2.15 (3H, s, CH₃), 2.21 (3H, s, CH₃), 1.50 (3H, s, CH₃ *trans* to C=O), 6.22 (1H, s, 4-thienyl proton) and 6.74, 7.13–7.57 (10H, m,

aromatics). The second crop of dark red crystals was (*Z*)-tetrahydrofuranone **10** (0.2 g, 12%), mp 173–175 °C (after recrystallisation from DCM and petrol). Found: C, 75.08; H, 4.27; N, 6.34; M^+ 448. $C_{28}H_{20}O_2N_2S$ requires C, 75.02; H, 4.46; N, 6.24%; M 448. λ_{\max} 330 nm, ϵ 16 220; δ_H 2.32 (3H, s, CH_3), 2.36 (3H, s, CH_3), 1.44 (3H, s, CH_3 *trans* to C=O), 6.44 (1H, s, 4-thienyl proton) and 6.74, 7.28–7.56 (10H, m, aromatics); ν_{\max}/cm^{-1} 2225 (CN) and 1706 (C=O).

Photorearrangement of (*Z*)-5-dicyanomethylene-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-diphenylmethylenetetrahydrofuran-2-one **10**

An NMR tube containing a deep red solution of (*Z*)-lactone **10** in deuteriochloroform was irradiated (3 days) at 366 nm (using the focussed beam of the 200 W mercury lamp) and the NMR spectrum measured. The spectrum showed that the solution contained a *ca.* 3:2 mixture of the maleic anhydride derivative **11** and starting (*Z*)-lactone **10**.

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References

- 1 A. M. A. Asiri, H. G. Heller, M. B. Hursthouse and A. Karalulov, *Chem. Commun.*, 2000, 799.
- 2 H. Meyer, *Chem. Ber.*, 1909, **42**, 143; A. Schönberg, F. A. Ismail and W. Asker, *J. Chem. Soc.*, 1942, 272; A. Schönberg, F. A. Ismail and W. Asker, *J. Chem. Soc.*, 1946, 442; A. Schönberg, M. Elkaschef, M. Nosseir and M. M. Sidky, *J. Am. Chem. Soc.*, 1958, **80**, 6312; G. Kortum, W. Theilhacker and G. Schreyer, *Z. Phys. Chem.*, 1957, **11**, 182; K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 556; K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 2057; K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 685; K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 2203; K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 429; T. Hayashi and M. Moriga, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 1563; K. Maeda, T. Hayashi and T. Kanaji, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 857; K. Maeda, A. Chinone and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1431; D. M. White and J. Sonnenberg, *J. Org. Chem.*, 1964, **29**, 1925; D. M. White and J. Sonnenberg, *J. Am. Chem. Soc.*, 1966, **88**, 3825; S. M. Blinder, M. L. Peller, N. W. Lord, L. C. Aamodt and N. S. Invanchukov, *J. Chem. Phys.*, 1962, **36**, 540; F. Kehrmann and Zd. Matusinsky, *Chem. Ber.*, 1912, **45**, 3498; N. Campbell and A. G. Cairns, *J. Chem. Soc.*, 1961, 1191; M. Matsui, K. Shibata and H. Muramatsu, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1845.
- 3 H. G. Heller, D. S. Hughes, M. B. Hursthouse and K. V. S. Koh, *J. Chem. Soc., Chem. Commun.*, 1994, 2713.
- 4 J. A. Moore and J. H. Khim, *Tetrahedron Lett.*, 1991, **32**, 3449.