

Photochemical Dimerization of Methyl 2-Furyl- and 2-Thienylacrylate and Related Compounds in Solution

Maurizio D'Auria,* Giovanni Piancatelli and Anna Vantaggi

Centro CNR per lo Studio della Chimica delle Sostanze Organiche Naturali, Dipartimento di Chimica, Università di Roma 'La Sapienza,' P. le A. Moro, 2, 00185 Roma, Italy

Irradiation of methyl 3-(2-furyl)acrylate **1** in the presence of benzophenone led to the formation of a mixture of *t*-3,4- and *c*-3,4-dimethyl 3,4-di-(2-furyl)cyclobutane-*r*-1,*c*-2-dicarboxylates **2** and **3** in 2:1 ratio and 90% overall yield. The reaction is an efficient synthetic method when using the corresponding acid **4**, the acrylaldehyde derivative **7a** and the corresponding methyl ketone **7b** as well. On the other hand the presence of a methyl group on the double bond inhibited the reaction, while the presence of a methyl group on the furan ring also depressed the reactivity of the double bond, giving only a 27% yield of the corresponding dimer. Methyl 3-(2-thienyl)acrylate **13** gave a mixture of two dimers **14** and **15** in an overall yield of 25%, while methyl cinnamate showed only *E-Z* isomerization.

During our researches devoted to the study of the photochemical reactivity of heterocycles,¹ we have tested the photochemical behaviour of heterocyclically substituted acrylic derivatives. The results of this work could give interesting information on the photochemical interaction between aryl-substituted olefins and halogeno-thiophene and -furan derivatives.²

In this paper we report our results concerning the dimerization of heterocyclic derivatives of cinnamic acid in acetonitrile solution.

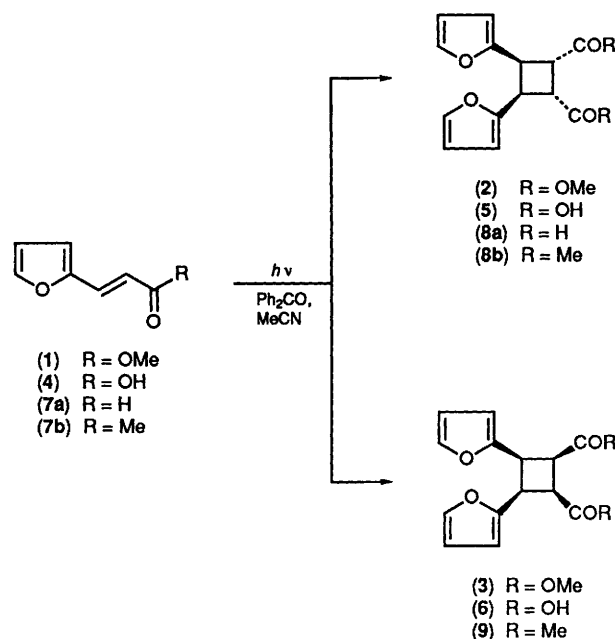
Results and Discussion

Irradiation of methyl 3-(2-furyl)acrylate **1** in acetonitrile in the presence of benzophenone as sensitizer furnished a mixture of two compounds, **2** and **3**, in 61 and 27% yield, respectively (Table 1). The ¹H NMR spectrum of compound **2** showed a doublet of doublets at δ_H 7.32, a doublet of doublets at δ_H 6.25, and a doublet at δ_H 6.12 (furyl protons), a singlet at δ_H 3.68 (CO₂Me), and an A₂X₂ system at δ_H 3.74 (*J*_{AX} 10 Hz) and at 3.51 (*J*_{AX} 10 Hz). The observed *J*-value was in agreement with a *trans* relationship between the cyclobutane protons as reported in β -truxinic acid.³ This completely symmetric structure was confirmed by the ¹³C NMR spectrum where we observed only eight carbon signals (multiplicity from DEPT experiments), at δ_C 172.1 (s, CO₂), 153.0 (s), 142.1 (d), 110.3 (d) and 106.6 (d) (furyl carbons), 52.1 (q, OMe), and 42.92 (d) and 39.57 (d, cyclobutane carbons).

Similarly, compound **3** showed ¹H NMR signals at δ_H 7.14, 6.11 and 5.87 (multiplets) relative to the furyl protons, a singlet at δ_H 3.65, and an A₂X₂ system at δ_H 4.17 and 3.79 (*J*_{AX} 7 Hz); this *J*-value is in agreement with a *cis* relationship between the cyclobutane protons. The ¹³C NMR spectrum confirmed the symmetric structure: in this case we again observed only eight signals, at δ_C 172.4 (s, CO₂), 152.7 (s), 141.8 (d), 110.2 (d) and 107.0 (d) (furyl carbons), 52.0 (q, OMe), 42.9 (d) and 38.3 (d).

The symmetric nature of the compounds was confirmed by their mass spectra, which showed a peak at *m/z* 304 (relative abundance 4%) and a parent peak at *m/z* 152: this behaviour is diagnostic for a head-to-head configuration of the substituents.^{4,5}

Similar results were obtained by using the corresponding acid **4**: we obtained the cyclobutane derivative **5** together with its isomer **6** (yield 80%, Table 1).



The furyl acrylates **10** and **11**, with a methyl group respectively in an α -position to the carboxylic ester and in an α -position on the furan ring, showed different behaviour. While compound **10** did not give any photodimer, its isomer **11** furnished only the photodimer **12**, in 22% yield. We did not observe the formation of products of type **3**. The presence of substituents on the double bond seems to be incompatible with photodimer formation while, unexpectedly, substitution on the furan ring also depresses the reactivity of the double bond.

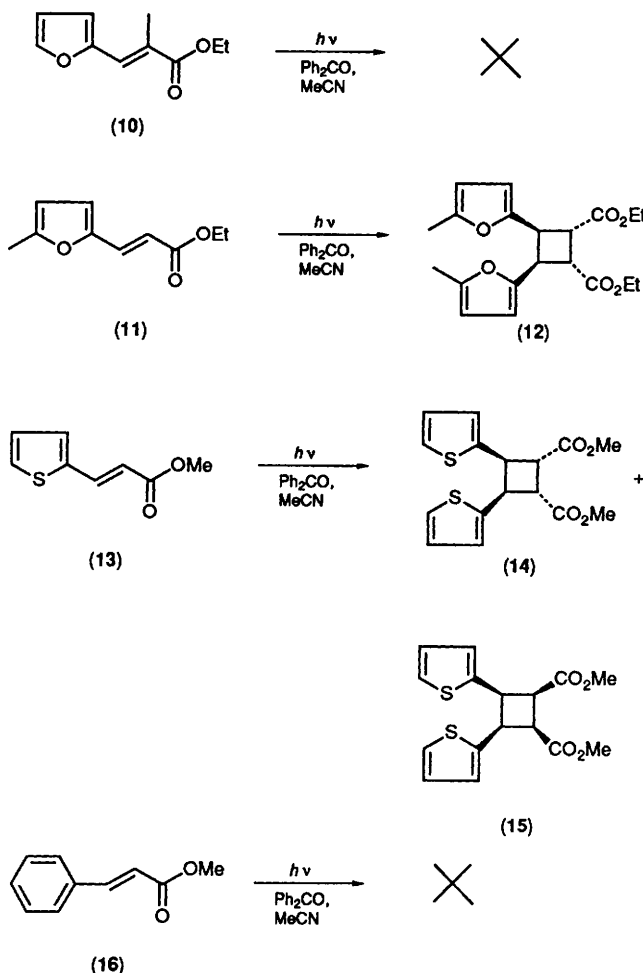
We then tested the reactivity of both the acrylaldehyde derivative **7a** and the methyl ketone **7b**. While the furylacrylaldehyde gave only the dimer **8a** in 42% yield, the photoreaction of ketone **7b** in the presence of benzophenone led to a 1:1 mixture of dimers **8b** and **9** in 70% overall yield (Table 1).

Finally, we wanted to verify the effect of a change in the nature of aromatic ring on the reactivity: for this purpose we used the thienyl derivative **13** and methyl cinnamate **16**.

Table 1. Photochemical dimerization of arylacrylic derivatives.

Entry	Substrate	Irradiation time (h)	Product	Yield (%) ^a
1	1	7	2 3	61 27
2	4	6	5 6	55 25
3	10	11	12	22
4	11	11	12	22
5	7	6	8a	42
6	7	5	8b 9	38 32
7	13	10	14 15	13 12
8	16	5		

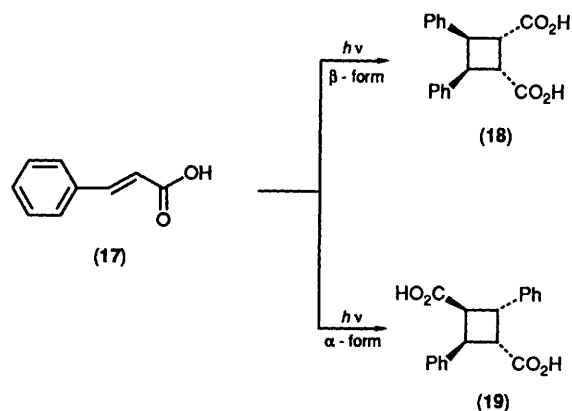
^a All yields refer to isolated, chromatographically pure products.



Compound **16** did not show any reactivity under our irradiation conditions, showing only the previously mentioned *E-Z* isomerization. The thienyl derivative **13** gave a mixture of two cyclobutane derivatives **14** and **15** in 1:1 ratio but we obtained these compounds with an overall yield of 25%.

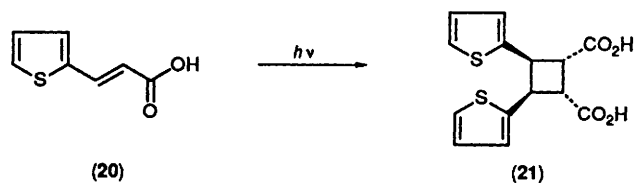
The photochemical dimerization of cinnamic acid has been known for 70 years.^{6,7} Cinnamic acid **17**, irradiated in the solid state, gave the corresponding photodimer depending on the crystal form of the starting material: the metastable β -form is reported to yield β -truxinic acid **18**, while the stable α -form gave α -truxillic acid **19**.^{8,9}

This type of reaction can also be performed on 3-(2-furyl)-

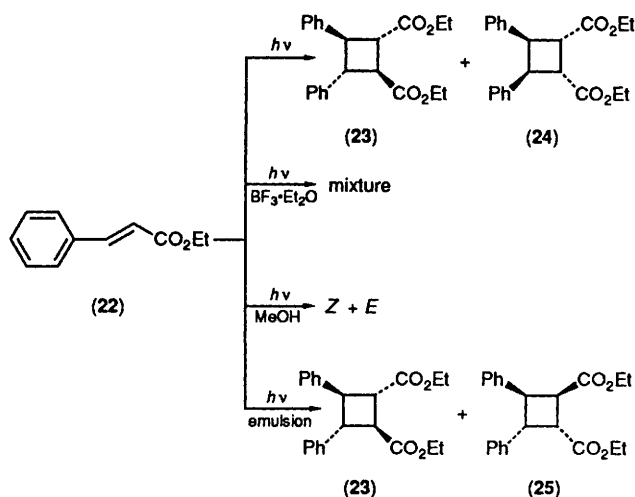


acrylic acid **4** or with 3-(2-thienyl)acrylic acid **20** to give the corresponding photodimers **5** and **21** if the irradiation is performed in the solid state.¹⁰ It is noteworthy that these reactions need 30 and 20 days of irradiation, respectively, to give the products.

Irradiation of the acids **4** and **20** in solution (MeOH) showed only *E-Z* isomerization of the starting materials.¹¹



While the reactivity of cinnamic acid is well defined, the reactivity of the esters is more complex. Irradiation of liquid ethyl cinnamate **22** furnished a mixture of two compounds **23** and **24** in 55 and 25% yield, respectively.¹² When the reaction was performed in a mixture of water (82.1%), cyclohexane (3.2%), butanol (9.8%), and sodium dodecyl sulphate (4.9%) an 8:2 mixture of *trans*-diesters **23** and **25** was obtained.¹³ On the other hand, irradiation in methanolic solution did not furnish any cyclodimerization product, giving instead only *E-Z* isomerization,¹⁴ while irradiation in the presence of BF_3 furnished a mixture of seven dimers.¹⁵



We have found that the photodimerization of furan-acrylic derivatives in solution is possible in contrast to the reported data for cinnamic acid derivatives. The observed order of reactivity is furan > thiophene \gg benzene, in the reverse order of aromaticity.

The reaction is extremely sensitive to steric hindrance on both the double bond and on the furan ring. This behaviour can be explained if complete superposition of two molecules is needed in order to initiate the reaction. Our photochemical reactions furnished dimers with high stereospecificity. In contrast with the complex mixtures obtained with ethyl cinnamate,¹⁵ we obtained only two head-to-head dimers and only the symmetric isomers. The use of acetonitrile can explain the formation of head-to-head dimers: it is known that in enone dimerization excited charge-transfer complexes can be involved. The formation of charge-transfer complexes, favoured in polar solvents, results in a predominance of head-to-head dimers.¹⁶ In contrast, the topochemical justifications used for the reactions in the solid state are useless for justification of the observed stereochemistry in our experiments.

The quantum yield of the conversion **7b** → **8b** + **9** was 0.078 ± 0.002 and was determined by the use of phenylglyoxylic acid as actinometer¹⁷ at 350 nm. As regards the sensitizer, acetone (E_T 79–82 kcal mol⁻¹)* and acetophenone (E_T 74.1 kcal mol⁻¹)¹⁸ were unable to induce the reaction as well as did benzophenone (E_T 69.2 kcal mol⁻¹).¹⁸ It is noteworthy that the dimerization did not work in the absence of benzophenone. The triplet energy of compound **7b** was estimated to be 52 kcal mol⁻¹ by using (*E*)-stilbene isomerization.¹⁹

All the above reported data are in agreement with the hypothesis that the described reactions occur through a benzophenone-sensitized mechanism. Further investigations are needed to verify if benzophenone has the same role as that shown in coumarin dimerization.²⁰

Experimental

M.p.s were obtained with a Mettler FP81 cell equipped with a Mettler FP80 Central Processor ¹H and ¹³C NMR spectra were recorded with Varian Gemini 200 MHz and with Varian XL300 spectrometers, with CDCl₃ as solvent. Mass spectra were obtained with a Kratos MS-80 instrument by direct insertion at a source temperature of 150 °C. IR spectra were obtained on a Perkin-Elmer 457 spectrometer. GLC analyses were performed with Hewlett-Packard 5880A and 5890 instruments (flame-ionization detector). Commercial Merck silica gel was used for column chromatography.

Starting Materials.—3-(2-Furyl)acrylic acid **4** was converted into the methyl ester **1** by reaction of the corresponding acyl chloride²¹ with MeOH in the presence of pyridine.²² Ethyl 3-(2-furyl)-2-methylacrylate **10** was obtained by condensation between furan-2-carbaldehyde with ethyl propionate.²³ The same procedure was utilized to prepare ethyl 3-(5-methyl-2-furyl)acrylate **11**. 4-(2-Furyl)but-3-en-2-one **7b** was obtained through condensation between furan-2-carbaldehyde and acetone.²⁴ Methyl 3-(2-thienyl)acrylate **13** was prepared from the corresponding acid by reaction with acidic MeOH.²⁵

(*E*)-Methyl 3-(2-Furyl)acrylate **1**.—B.p. 114–116 °C/18 mmHg (lit.,²⁶ 114–115 °C/16 mmHg); δ_H 7.50 (1 H, m), 7.10 (1 H, d, *J* 16 Hz), 6.59 (1 H, d, *J* 4 Hz), 6.44 (1 H, dd, *J*₁ 2, *J*₂ 4 Hz), 6.29 (1 H, d, *J* 16 Hz) and 3.77 (3 H, s); ν_{max} 1720, 1645, 1560, 1485, 1435, 1390, 1310, 1275, 1260, 1210, 1200, 1168, 1075, 1040, 1020, 970, 930, 883, 860, 818, 750, 730 and 680 cm⁻¹; *m/z* 152.

(*E*)-Ethyl 3-(2-Furyl)-2-methylacrylate **10**.—B.p. 102–105 °C/5 mmHg (lit.,²³ 103–104 °C/4.5 mmHg); δ_H 7.50 (1 H, d, *J* 1.7 Hz), 7.41 (1 H, m), 6.58 (1 H, d, *J* 3.5 Hz), 6.47 (1 H, dd, *J*₁ 1.7, *J*₂ 3.5 Hz), 4.22 (2 H, q, *J* 7 Hz), 2.19 (3 H, s) and 1.31 (3 H, t,

J 7 Hz); ν_{max} 1695, 1630, 1368, 1150, 1110, 1082, 1012 and 885 cm⁻¹; *m/z* 180.

(*E*)-Ethyl 3-(5-Methyl-2-furyl)acrylate **11**.—B.p. 146–148 °C/30 mmHg (lit.,²⁷ 128–130 °C/16–18 mmHg); δ_H 7.33 (1 H, d, *J* 15.7 Hz), 6.47 (1 H, d, *J* 3 Hz), 6.20 (1 H, d, *J* 15.7 Hz), 6.04 (1 H, dd, *J*₁ 3, *J*₂ 0.9 Hz), 4.20 (2 H, q, *J* 7 Hz), 2.31 (3 H, s) and 1.28 (3 H, t, *J* 7 Hz); ν_{max} 1718, 1645, 1590, 1530, 1370, 1310, 1260, 1193, 1162, 1025 and 975 cm⁻¹; *m/z* 180.

(*E*)-4-(2-Furyl)but-3-en-2-one **7b**.—B.p. 130–135 °C/30 mmHg (lit.,²⁴ 114–118 °C/10 mmHg); δ_H 7.48 (1 H, d, *J* 1.8 Hz), 7.25 (1 H, d, *J* 15.9 Hz), 6.64 (1 H, d, *J* 3.5 Hz), 6.59 (1 H, d, *J* 15.9 Hz), 6.46 (1 H, dd, *J*₁ 3.5, *J*₂ 1.8 Hz) and 2.30 (3 H, s); ν_{max} 1700, 1675, 1620, 1480, 1390, 1360, 1320, 1305, 1285, 1250, 1205, 1170, 1100, 1020, 970, 930, 910 and 885 cm⁻¹; *m/z* 136.

(*E*)-Methyl 3-(2-Thienyl)acrylate **13**.—M.p. 41–42 °C (lit.,²⁸ 40–42.2 °C); δ_H 7.76 (1 H, d, *J* 15.7 Hz), 7.34 (1 H, d, *J* 5 Hz), 7.22 (1 H, d, *J* 3.7 Hz), 7.02 (1 H, dd, *J*₁ 5, *J*₂ 3.7 Hz), 6.21 (1 H, d, *J* 15.7 Hz) and 3.75 (3 H, s); ν_{max} 1730, 1635, 1440, 1430, 1365, 1310, 1268, 1202, 1168, 1045, 970, 928 and 860 cm⁻¹; *m/z* 168.

Synthesis of Cyclobutane Derivatives. General Procedure.—An alkene **1**, **4**, **7**, **10**, **11**, **13**, or **16** (1 g) was dissolved in acetonitrile (300 ml) in the presence of benzophenone (100 mg). The solution was outgassed with nitrogen for 1 h and was then irradiated in an immersion apparatus with a 500 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. At the end of the reaction (Table 1), removal of the solvent under reduced pressure yielded a crude product, which was chromatographed on silica gel. The following compounds were thus prepared.

Dimethyl *t*-3,4-Di-(2-furyl)cyclobutane-*r*-1,*c*-2-dicarboxylate **2**.—Very dense oil (Found: C, 63.5; H, 5.2. C₁₆H₁₆O₆ requires C, 63.15; H, 5.30%); δ_H 7.32 (1 H, dd, *J*₁ 2, *J*₂ 1 Hz), 6.25 (1 H, dd, *J*₁ 3, *J*₂ 2 Hz), 6.12 (1 H, d, *J* 3 Hz), 3.74 (1 H, m, *J* 10 Hz), 3.68 (3 H, s) and 3.51 (1 H, m, *J* 10 Hz); δ_C 172.06 (s), 153.02 (s), 142.13 (d), 110.27 (d), 106.58 (d), 52.08 (q), 42.92 (d) and 39.56 (d); ν_{max} 1735, 1600, 1440, 1380, 1150, 1010, 950 and 885 cm⁻¹; *m/z* 304.

Dimethyl *c*-3,*c*-4-Di-(2-furyl)cyclobutane-*r*-1,*c*-2-dicarboxylate **3**.—Very dense oil (Found: C, 62.8; H, 5.2%); δ_H 7.14 (1 H, m), 6.11 (1 H, m), 5.87 (1 H, m), 4.17 (1 H, m, *J* 7 Hz), 3.79 (1 H, m, *J* 7 Hz) and 3.65 (3 H, s); δ_C 172.38 (s), 152.66 (s), 141.80 (d), 110.21 (d), 106.97 (d), 52.01 (q), 42.92 (d) and 38.31 (d); ν_{max} 1740, 1600, 1505, 1440, 1360, 1320, 1285, 1205, 1170, 1150, 1075, 1015, 910 and 885 cm⁻¹; *m/z* 304.

t-3,*t*-4-Di-(2-furyl)cyclobutane-*r*-1,*c*-2-dicarboxylic Acid **5**.—M.p. 177–178 °C (lit.,¹⁰ 179–179 °C) (Found: C, 61.0; H, 4.2. Calc. for C₁₄H₁₂O₆: C, 60.87; H, 4.38%); δ_H 7.35 (1 H, m), 6.38 (1 H, m), 6.17 (1 H, m), 3.82 (1 H, m, *J* 10 Hz) and 3.58 (1 H, m, *J* 10 Hz); *m/z* 276.

c-3,*c*-4-Di-(2-furyl)cyclobutane-*r*-1,*c*-2-dicarboxylic Acid **6**.—Syrup (Found: C, 60.6; H, 4.3%); δ_H 7.48 (1 H, m), 7.20 (1 H, m), 5.94 (1 H, m), 4.24 (1 H, m, *J* 7 Hz) and 3.93 (1 H, m, *J* 7 Hz); *m/z* 276.

Diethyl *t*-3,*t*-4-Bis-(5-methyl-2-furyl)cyclobutane-*r*-1,*c*-2-dicarboxylate **12**.—Very dense oil (Found: C, 66.7; H, 6.9. C₂₀H₂₄O₆ requires C, 66.75; H, 6.71%); δ_H 5.99 (1 H, d, *J* 3 Hz), 5.83 (1 H, dd, *J*₁ 3, *J*₂ 1 Hz), 4.16 (2 H, q, *J* 7 Hz), 3.66 (1 H, m, *J* 10 Hz), 3.41 (1 H, m, *J* 10 Hz), 2.24 (3 H, s) and 1.23 (3 H, t,

* 1 cal = 4.184 J.

J 7 Hz); ν_{\max} 1730, 1620, 1570, 1450, 1370, 1320, 1300, 1155, 1100, 1020, 910 and 860 cm^{-1} ; m/z 360.

t-3,t-4-Di-(2-furyl)cyclobutane-r-1,c-2-dicarbaldehyde 8.—Very dense oil (Found: C, 69.0; H, 4.8. $\text{C}_{14}\text{H}_{12}\text{O}_4$ requires C, 68.85; H, 4.95%); δ_{H} 9.80 (1 H, s), 7.35 (1 H, d, J 1.8 Hz), 6.29 (1 H, dd, J_1 3.2, J_2 1.8 Hz), 6.14 (1 H, d, J 3.2 Hz), 3.80 (1 H, m, J 9.6 Hz) and 3.67 (1 H, m, J 9.6 Hz); ν_{\max} 2720, 1725, 1605, 1383, 1150, 1010 and 885 cm^{-1} ; m/z 244.

r-1,c-2-Diacetyl-t-3,t-4-di-(2-furyl)cyclobutane 8b.—Very dense oil (Found: C, 70.4; H, 6.1. $\text{C}_{16}\text{H}_{16}\text{O}_4$ requires C, 70.59; H, 5.92%); δ_{H} 7.33 (1 H, dd, J_1 1.8, J_2 0.8 Hz), 6.27 (1 H, dd, J_1 3.3, J_2 1.8 Hz), 6.13 (1 H, dd, J_1 3.3, J_2 0.8 Hz), 3.58 (2 H, s) and 2.07 (3 H, s); ν_{\max} 1700, 1600, 1355, 1145, 1010 and 880 cm^{-1} ; m/z 272.

r-1,c-2-Diacetyl-c-3,c-4-di-(2-furyl)cyclobutane 9.—Very dense oil (Found: C, 70.3; H, 6.1%); δ_{H} 7.21 (1 H, d, J 1.8 Hz), 6.19 (1 H, dd, J_1 3.2, J_2 1.8 Hz), 5.91 (1 H, d, J 3.2 Hz), 4.03 (1 H, m, J 7 Hz), 3.89 (1 H, m, J 7 Hz) and 2.15 (3 H, s); ν_{\max} 1710, 1600, 1365, 1150, 1015 and 885 cm^{-1} ; m/z 272.

Dimethyl t-3,t-4-Di-(2-thienyl)cyclobutane-r-1,c-2-dicarboxylate 14.—Very dense oil (Found: C, 57.2; H, 4.9. $\text{C}_{16}\text{H}_{16}\text{O}_4\text{S}_2$ requires C, 57.12; H, 4.79%); δ_{H} 7.19 (1 H, dd, J_1 3.9, J_2 2.5 Hz), 6.96 (2 H, m), 3.82 (1 H, m, J 9.6 Hz), 3.72 (3 H, s) and 3.44 (1 H, m, J 9.6 Hz); ν_{\max} 1730, 1625, 1435, 1170, 1030, 920, 880 and 845 cm^{-1} ; m/z 336.

Dimethyl c-3,c-4-Di-(2-thienyl)cyclobutane-r-1,c-2-dicarboxylate 15.—Very dense oil (Found: C, 57.0; H, 4.9%); δ_{H} 7.06 (1 H, dd, J_1 5.1, J_2 1.2 Hz), 6.82 (1 H, dd, J_1 5.1, J_2 3.5 Hz), 6.70 (1 H, dd, J_1 3.5, J_2 1.2 Hz), 4.50 (1 H, m, J 6 Hz), 3.78 (1 H, m, J 6 Hz) and 3.71 (3 H, s); ν_{\max} 1730, 1610, 1440, 1375, 1320 and 1165 cm^{-1} ; m/z 336.

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