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Highly facile and stereoselective intramolecular [2+2]photocycloadditions of bis(alkenoyl)ketenedithioacetals

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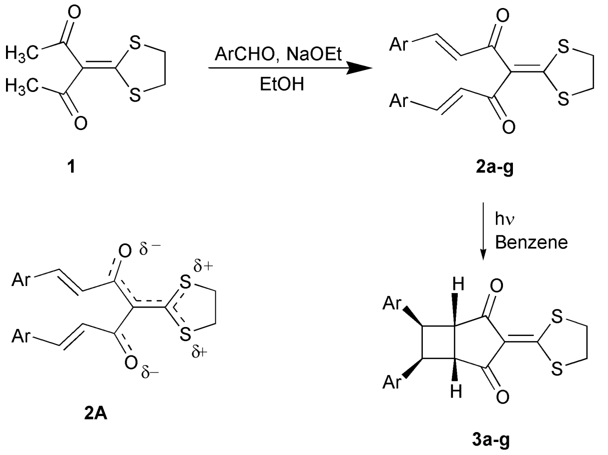
The conformational change induced by the introduction of a ketenedithioacetal moiety at C-4 of 1,7-substituted-1,6-heptadiene-3,5-diones results in favorable spatial relationships between the alkenoyl groups to effect efficient intramolecular cycloadditions: irradiation of bis(alkenoyl)ketenedithioacetals in solution leads to facile and stereospecific intramolecular [2 + 2] photocycloadditions resulting in the formation of substituted bicyclo[3.2.0]heptane-2,4-diones, the observed conformational rigidity of which is attributed to the *push–pull* character of the ketenedithioacetal group.

Over the years, the photochemistry of cinnamic acid derivatives has attracted interest owing to their applications as photosensitive groups in polymer materials, molecular assemblies and UV filters.[1] While *trans*-cinnamic acid and cinnamates photodimerize readily in the crystalline state, in solution they undergo mostly *cis–trans* isomerisation. Though intramolecular [2+2] cycloadditions of cinnamate groups linked by spacers[2] have been reported, the double bonds are far apart when fewer numbers of atoms separate them, unless they are brought close to each other due to the geometrical constraints in the substrate. Recently, in an effort to transfer the topochemical control of the crystalline state to solution, appropriately substituted [2,2] paracyclophane derivatives have been shown to undergo efficient stereospecific intramolecular [2 + 2] addition of the cinnamate groups.[3] Banwell *et al.* have elegantly used the change in the geometrical relations induced by the introduction of a cyclopropyl group to a *syn*-cyclopropylidene dimer to bring two *p*-benzoquinone moieties close enough to effect intramolecular [2 + 2] cycloaddition.[4] In this communication, we show that the *push–pull* character of polarized ketenedithioacetal group can bring about favorable spatial relationships between the double bonds of bis(cinnamoyl)ketenedithioacetals to effect efficient and stereospecific intramolecular photochemical [2 + 2] cycloadditions in solution.

The bis(alkenoyl)ketenedithioacetals **2a–g** were readily available by the Claisen–Schmidt condensation of 3-(1,3-dithiolane-2-yliden)pentane-2,4-dione **1** with aromatic aldehydes (Scheme 1). The crystal structure of bis(cinnamoyl)ketenedithioacetal (Fig. 1) shows that the cinnamoyl groups are aligned parallel and close to each other. The carbon atoms α to the carbonyl groups are separated by just 2.9 Å. The crystal studies on 1,6-heptadiene-3,5-diones, having an unsubstituted methylene group show that they have a linear structure as should be expected due to the keto–enol tautomerisation.[5] Thus the conformational change induced by the simple introduction of the cyclic ketenedithioacetal group brings the double bonds spatially close enough for an effective intramolecular photochemical [2 + 2] cycloaddition. The parallel alignment of the cinnamoyl group in bis(cinnamoyl)ketenedithioacetal apparently results from the *push–pull* nature of the ketenedithioacetal group. The delocalization of the electrons would result in developing partial negative charges on oxygen atom and partial positive charges on sulfur atoms as indicated in **2A**. This is supported by the observed bond lengths in the crystal structure of **2a** and also by the fact that both the carbonyl groups as well as the carbon and sulfur atoms of the ketenedithioacetal moiety lie on the same plane.



a, A r = C_6H_5 (50%) **b**, Ar = 4-$MeOC_6H_4$ (55%)
c, A r = 4-ClC_6H_4 (57%) **d**, Ar = 3-$MeOC_6H_4$ (62%)
e, Ar = 2-$MeOC_6H_4$ (55%) **f**, Ar = 3,4-$(MeO)_2C_6H_3$ (70%)
g, Ar = thienyl (40%)

Scheme 1

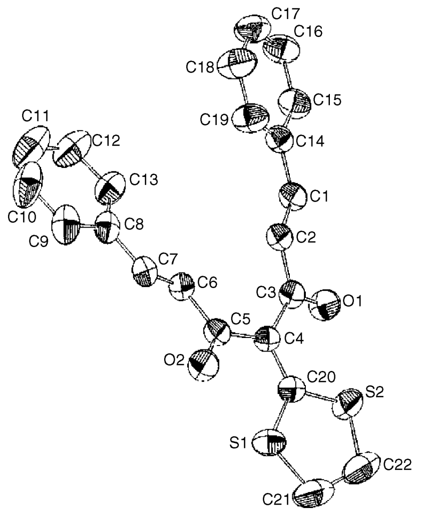


Fig. 1 ORTEP drawing of 4-(1,3-dithiolan-2-yliden)-1,7-diphenyl-1,6-heptadiene-3,5-dione **2a**.

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Irradiation of a solution of the bis(cinnamoyl)ketenedithioacetal **2a** in benzene (2.5 × 10^{-3} M) with Pyrex filtered light for one hour gave bicyclo[3,2,0]heptane-2,4-dione **3a** as a yellow crystalline solid (mp. 170–173 °C) as the only product in 50% isolated yield, while rest of the starting material could be recovered unchanged (Scheme 1).

Irradiation of a more dilute solution (2.75 × 10^{-5} M) of **2a** has resulted in complete conversion into **3a** in less than five min (Fig. 2).

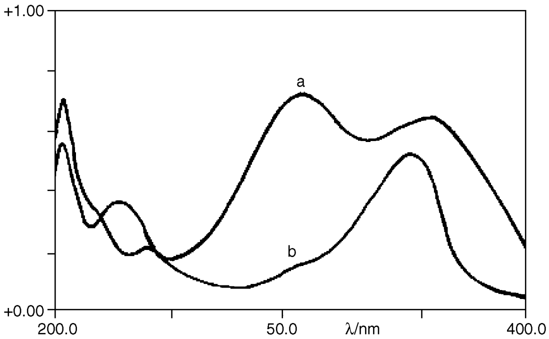

Fig. 2 Electronic absorption spectra of **2a** (2.75 × 10^{-5} M) in methanol before (**a**) and after irradiation for 5 minutes at > 300 nm (**b**).

The structure of the product **3a** was determined on the basis of spectral and analytical data.[6] Finally the stereochemical features were established by X-ray structural analysis (Fig. 3).† Similarly, the other 1,7-disubstituted-4-(1,3-dithiolan-2-ylidene)-1,6-heptadiene-3,5-diones **2b–g** also gave the respective bicyclo[3,2,0]heptane-2,4-diones **3b–g** in 40–70% overall yields (Scheme 1). The structures of the products **3b** and **3c** were confirmed with the help of spectral and analytical data.

In conclusion, we have developed a very facile method for exerting topochemical control over cycloaddition reactions of the cinnamoyl groups by the incorporation of a ketenedithioacetal moiety. It was found that the *push–pull* nature of the ketenedithioacetal functionality organizes the cinnamoyl groups parallel and close to each other, thereby effecting a facile internal photochemical [2 + 2] cycloaddition. Studies on other possible transformations induced by the conformational rigidity of polarized ketenedithioacetals as well as the likely applications of the highly functionalized bicycloheptanediones **3** are in progress.

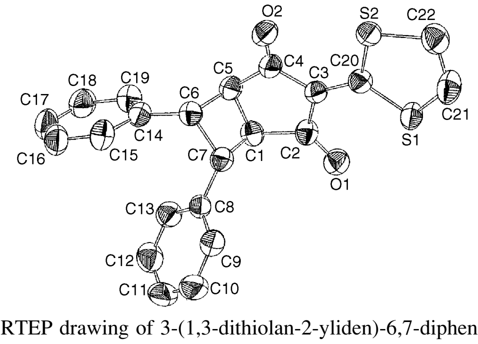

Fig. 3 ORTEP drawing of 3-(1,3-dithiolan-2-yliden)-6,7-diphenylbicyclo[3.2.0]heptane-2,4-dione **3a**.

Notes and references

† *Crystal data for* **2a**: Yellow prismatic crystal, $C_{22}H_{18}O_2S_2$, monoclinic space group $P2_1/c$, a = 8.998(4), b = 16.579(6), c = 13.372(6) Å, β = 106.50(5)°, V = 1913(1) Å^3, Z = 4, D_c = 1.314 g cm^{-3}, μ = (Cu-Kα) = 2.63 cm^{-1}. The structure was solved by direct method and refined on $|F|^2$ by full-matrix least-squares refinement using the program SHELX-97.[7] The final R and Rw were 0.051 and 0.139, respectively, using 3267 unique reflections with $I > 2\sigma(I)$. GoF = 1.05. CCDC 169427.

Crystal data for **3a**: Yellow needle like crystal, $C_{22}H_{18}O_2S_2$, orthorhombic space group $Pna2_1$, a = 31.600(7), b = 5.630(1), c = 10.199(6) Å, V = 1814(1) Å^3, Z = 4, D_c = 1.385 g cm^{-3}, μ = (Cu-Kα) = 2.76 cm^{-1}. The structure was solved by direct method and refined on $|F|^2$ by full-matrix least-squares refinement using the program SHELX-97.[7] The final R and Rw were 0.0479 and 0.1263, respectively, using 1501 unique reflections with $I > 2\sigma(I)$. GoF = 1.143. CCDC 169428. See http://www.rsc.org/suppdata/cc/b2/b200395n/ for crystallographic files in .cif format.

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6 3-(1,3-Dithiolan-2-yliden)-6,7-diphenyl bicyclo[3,2,0]heptane-2,4-dione **3a**. Obtained as a yellow crystalline solid by the irradiation of 400 mL of 2.5 × 10^{-3} M solution of **2a** for 1 h . Yield (20 mg, 50%), mp 170–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.5 (4H, s, SCH_2), 3.6 (2H, d, cyclobutane), 4.1 (2H, d, cyclobutane), 6.9–7.3 (10H, m, aromatic) ppm. ^{13}C NMR (300 MHz, $CDCl_3$) δ 29.1, 37.7, 46.8, 47.2, 47.8, 48.6, 109.2, 127.8, 138.9, 200.9 ppm. IR ν_{max}/cm^{-1} 1625, 1440, 1285, 1225. FAB mass 379 (M^+ + 1, 95%), 199 (90%), 165 (24%), 155 (50%), 149 (30%), 138 (58%), 57 (100%), Anal. Calcd. for $C_{22}H_{18}O_2S_2$ C, 69.81; H, 4.79; Found C, 69.72; H, 4.86%.

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