

Cycloadditions of Ketene Acetals under Microwave Irradiation in Solvent-free Conditions

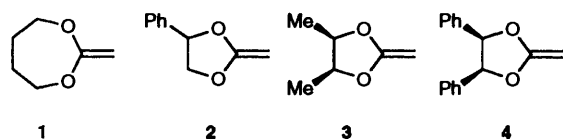
Angel Díaz-Ortiz,* Enrique Díez-Barra, Antonio de la Hoz, Pilar Prieto and Andrés Moreno
Facultad de Química, Universidad de Castilla-La Mancha, E-13071, Ciudad Real, Spain

When subjected to microwave irradiation ketene acetals undergo 1,3-dipolar and hetero-Diels–Alder cycloadditions within 5–12 min to give excellent yields of easily purified heterocyclic products. This efficient and rapid synthesis has the advantage of employing milder reaction conditions than those of classical thermal heating.

1,3-Dipolar and hetero-Diels–Alder cycloadditions, two of the best and most widely used syntheses for five- and six-membered heterocycles,¹ involve, in most cases, a 1,3-dipole or hetero-1,3-diene and an alkene. We have recently reported a simple and efficient synthesis of cyclic ketene acetals by phase-transfer catalysis without solvent coupled with ultrasound.² Ketene acetals have been widely employed as dipolarophiles³ and dienophiles,⁴ but their cycloadditions under classical thermal conditions are generally performed at high temperatures (> 100 °C) with long reaction times (several hours or days) and sometimes carried out under an inert atmosphere.

In recent years, domestic microwave ovens have been used as controllable thermal sources to improve many organic reactions,⁵ by decreasing the reaction times (up to 3 orders of magnitude) and, in some cases, giving cleaner reactions with easier work-up. Reactions in the absence of solvent have also made it possible to work in open vessels, thus avoiding the risk of high pressures and explosions, and to carry out reactions on a preparative scale.⁶ Such conditions have been applied, with or without solvent, to Diels–Alder,⁷ 1,3-dipolar⁸ and [2 + 2]⁹ cycloadditions, improving reaction times and often yields dramatically. In these reactions reagents were generally stable. This technique, however, had not been used with unstable compounds such as cyclic ketene acetals that polymerize easily.

We have attempted, by using microwave irradiation under solvent-free conditions, to induce 1,3-dipolar and hetero-Diels–Alder cycloadditions of cyclic ketene acetals under milder reaction conditions than those reported in the literature.^{3,4} In our work we used compounds 1–4 to study their reactions with



several 1,3-dipoles (e.g. nitrones and nitrile oxides) and hetero-1,3-dienes (e.g. α,β -unsaturated ketones). The results are summarized in Table 1.

We found that microwave irradiation induces ketene acetals to react with 1,3-dipoles and hetero-1,3-dienes under solvent-free conditions within a few minutes to give the corresponding cycloadducts. Reaction times are dramatically reduced, yields are excellent and products are isolated directly from the crude reaction mixture by column chromatography; further, no polymerization of ketene acetals was observed. It has, therefore, been demonstrated that microwave irradiation is an efficient technique for 1,3-dipolar and hetero-Diels–Alder cycloadditions with cyclic ketene acetals.

The structures of the cycloadducts were established on the basis of spectroscopic data. The multiplicity and coupling

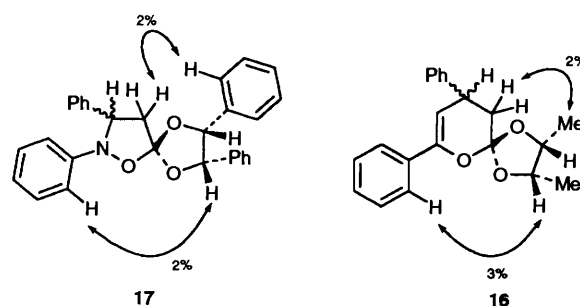


Fig. 1 Selected NOEs for compounds 17 and 16

constants of the signals corresponding to the 3- and 4-H, or 4- and 5-H, protons in their ¹H NMR spectra allowed the regiochemistry to be assigned for reactions with nitrones or α,β -unsaturated ketones, respectively. The chemical shift of C-4 (30–45 ppm) suggests that the regiochemistry with nitrile oxides is the one shown in Table 1.

Although cycloaddition of the unsubstituted ketene acetal 1 gave only one adduct, with the acetal 2 the Ph group in the adducts may exist either 'up' or 'down' with respect to the dioxolane ring, depending upon the approach of the reagents. In cycloadditions of compound 4 there is only one approach resulting from the increased steric hindrance at the 'top' face of the ketene acetal. Since 4 is achiral (*meso*) the adducts 17–20 were obtained as a racemic mixture. The stereochemical disposition of the dioxolane ring substituents has been inferred by NOE difference experiments (see Fig. 1). The small steric volume of the methyl substituents in the acetal 3 permits the cycloaddition of *C,N*-diphenylnitron to occur from two directions. Structural disposition of the dioxolane ring in the cycloadducts has been inferred again by NOE difference experiments. The major isomer 14 showed an NOE signal for 3- and 4-H when the methyl groups were irradiated. The minor isomer 15 did not show this. Contrary to what was expected, reaction of 3 with chalcone afforded only one adduct, 16.

Experimental

All m.p.s were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer 883 instrument. ¹H NMR spectra were either recorded at 300 MHz on a Varian Unity 300 or at 200 MHz on a Varian Gemini spectrometer. ¹³C NMR spectra were recorded at 75 MHz on a Varian Unity 300 machine. Chemical shifts are reported in ppm (δ) using Me₄Si as standard, and coupling constants *J* are given in Hz. Percentage NOE enhancements were obtained by integrating the affected resonance relative to the irradiated resonance in the difference spectrum in each case. Elemental

Table 1

	Reaction ^a	Conditions	Products	Yield (%) ^b
1 +		MW, 780 W 12 min		78
1 +		MW, 780 W 10 min		81
1 +		MW, 450 W 5 min		70
1 +		MW, 450 W 5 min		88
1 +		MW, 780 W 15 min		92
2 +		MW, 450 W 5 min		72
2 +		MW, 780 W 10 min		86
3 +		MW, 780 W 10 min		88
3 +		MW, 780 W 10 min		73
4 +		MW, 780 W 10 min		95
4 +		MW, 780 W 10 min		79
4 +		MW, 780 W 10 min		69
4 +		MW, 780 W 10 min		91

^a Equimolecular amounts. ^b Isolated product.

analyses were performed on a Perkin-Elmer PE2400 CHN elemental analyser. Column chromatography was carried out with SiO₂ (silica gel, Merck type 60 70–230 and 60 230–400 mesh). Microwave irradiations were conducted in a Miele Electronic M720 domestic oven. Reagents were purchased from commercial suppliers or prepared by literature methods.

General Procedure for the 1,3-Dipolar and Hetero-Diels–Alder Cycloadditions of Ketene Acetals induced by Microwave Irradiation.—A mixture of the ketene acetal (1 equiv.) and 1,3-dipole or hetero-1,3-diene (1 equiv.) was placed in an open vessel in the microwave oven and irradiated at the power specified for the indicated time. The crude reaction mixture was purified by flash chromatography (silica gel) using light petroleum (40–60 °C)–ethyl acetate (7:1) as eluent, unless otherwise stated, to give the corresponding cycloadduct.

1,3-Dipolar Cycloaddition of the Ketene Acetal 1 with N-(Benzylidene)phenylamine N-Oxide.—The ketene acetal 1 (0.20 g, 1.75 mmol) and N-(benzylidene)phenylamine N-oxide¹⁰ (0.345 g, 1.75 mmol) when irradiated at 780 W for 12 min (final temp. 145 °C) gave the cycloadduct 5 (0.425 g, 78%); eluent: light petroleum (b.p. 40–60 °C)–ethyl acetate (10:1); m.p. 89–90 °C (Found: C, 73.2; H, 6.85; N, 4.4. Calc. for C₁₉H₂₁NO₃: C, 73.4; H, 6.8; N, 4.5%); ν_{\max} (KBr)/cm⁻¹ 3061 (=C–H), 1597 (C=C) and 1058 (C–O); δ_{H} (200 MHz; CDCl₃) 1.73 (4 H, m, 5'- and 6'-H), 2.48 (1 H, dd, *J* 12.2 and 9.4, 4a-H), 2.85 (1 H, dd, *J* 12.2 and 7.7, 4b-H), 3.66 (4 H, m, 4'- and 7'-H), 4.72 (1 H, dd, *J* 9.4 and 7.7, 3-H) and 6.89–7.52 (10 H, m, ArH).

1,3-Dipolar Cycloaddition of the Ketene Acetal 1 with N-(4-Trifluorobenzylidene)phenylamine N-Oxide.—The ketene acetal 1 (0.050 g, 0.45 mmol) and N-(4-trifluorobenzylidene)phenylamine N-oxide¹⁰ (0.116 g, 0.45 mmol) when irradiated at 780 W for 10 min (final temp. 110 °C) gave compound 6 (0.134 g, 81%), m.p. 133–134 °C (Found: C, 63.15; H, 5.3; N, 3.65. Calc. for C₂₀H₂₀F₃NO₃: C, 63.3; H, 5.3; N, 3.7%); ν_{\max} (KBr)/cm⁻¹ 3077 (=C–H), 1597 (C=C), 1109 (C–F) and 1085 (C–O); δ_{H} (200 MHz; CDCl₃) 1.73 (4 H, m, 5'- and 6'-H), 2.44 (1 H, dd, *J* 12.3 and 8.6, 4a-H), 2.88 (1 H, dd, *J* 12.3 and 8.1, 4b-H), 3.66 and 4.05 (4 H, 2 × m, 4'- and 7'-H), 4.81 (1 H, dd, *J* 8.6 and 8.1, 3-H) and 6.91–7.62 (9 H, m, ArH); δ_{C} (75 MHz; CDCl₃) 28.66 and 29.01 (C-5' and -6'), 46.65 (C-4), 64.18 and 65.19 (C-4' and -7'), 69.86 (C-3) and 115.46–151.14 (CF₃, C-5 and C-arom).

1,3-Dipolar Cycloaddition of Ketene Acetal 1 with 2,4,6-Trimethylbenzotrile Oxide.—The ketene acetal 1 (0.191 g, 1.68 mmol) and 2,4,6-trimethylbenzotrile oxide¹¹ (0.27 g, 1.68 mmol) when irradiated at 450 W for 5 min (final temp. 71 °C) gave the cycloadduct 7 (0.321 g, 70%), m.p. 82–83 °C (Found: C, 69.95; H, 7.7; N, 5.0. Calc. for C₁₆H₂₁NO₃: C, 69.9; H, 7.7; N, 5.1%); ν_{\max} (KBr)/cm⁻¹ 3001 (=C–H), 1608 (C=C), 1335 (N–O) and 1086 (C–O); δ_{H} (200 MHz; CDCl₃) 1.77 (4 H, m, 5'- and 6'-H), 2.25 (6 H, s, *ortho*-CH₃), 2.28 (3 H, s, *para*-CH₃), 3.10 (2 H, s, 4-H), 3.75 and 4.09 (4 H, 2 × m, 4'- and 7'-H) and 6.88 (2 H, s, ArH); δ_{C} (75 MHz; CDCl₃) 19.44 (*ortho*-CH₃), 20.95 (*para*-CH₃), 28.71 (C-5' and -6'), 45.75 (C-4), 64.81 (C-4' and -7') and 125.24–159.45 (C-3, -5 and C-arom).

1,3-Dipolar Cycloaddition of the Ketene Acetal 1 with 3,5-Dimethoxybenzotrile Oxide.—The ketene acetal 1 (0.092 g, 0.81 mmol) and 3,5-dimethoxybenzotrile oxide¹¹ (0.145 g, 0.81 mmol) when irradiated at 450 W for 5 min (final temp. 60 °C) gave product 8 (0.208 g, 88%), m.p. 123–125 °C (Found: C, 61.2; H, 6.4; N, 4.85. Calc. for C₁₅H₁₉NO₅: C, 61.4; H, 6.5; N, 4.75%); ν_{\max} (KBr)/cm⁻¹ 2998 (=C–H), 1606 (C=C) and 1372 (N–O); δ_{H} (200 MHz; CDCl₃) 1.70 (2 H, s, 4-H), 1.72 (4 H, m,

5'- and 6'-H), 3.73 and 4.02 (4 H, 2 × m, 4'- and 7'-H), 3.83 and 3.87 (6 H, 2 × s, CH₃O) and 6.5–7.2 (3 H, m, ArH); δ_{C} (75 MHz; CDCl₃) 21.97 (C-5' and -6'), 28.93 (C-4), 55.57 and 56.26 (CH₃O), 63.41 (C-4' and -7') and 101.56–159.34 (C-3, -5 and C-arom).

Hetero-Diels–Alder Cycloaddition of the Ketene Acetal 1 with Chalcone.—The ketene acetal 1 (0.15 g, 1.31 mmol) and chalcone (0.27 g, 1.31 mmol) when irradiated at 780 W for 15 min (final temp. 120 °C) gave the cycloadduct 9 (0.39 g, 92%), m.p. 101–102 °C (Found: C, 78.1; H, 6.95. Calc. for C₂₁H₂₂O₃: C, 78.25; H, 6.85%); ν_{\max} (KBr)/cm⁻¹ 3058 (=C–H), 1642 (C=C) and 1052 (C–O); δ_{H} (200 MHz; CDCl₃) 1.76 (5 H, m, 5a-, 5'- and 6'-H), 2.41 (1 H, ddd, *J* 12.2, 6.3 and 1.2, 5b-H), 3.75, 4.01 and 4.20 (5 H, 3 × m, 4-, 4'- and 7'-H), 5.50 (1 H, dd, *J* 2.4 and 1.2, 3-H) and 7.25–7.68 (10 H, m, ArH); δ_{C} (75 MHz; CD₃SOCD₃) 28.28 and 28.76 (C-5' and -6'), 36.88 and 37.26 (C-4 and -5), 62.10 and 62.92 (C-4' and -7'), 101.75 (C-3) and 113.63–148.26 (C-2, -6 and C-arom).

1,3-Dipolar Cycloaddition of Ketene Acetal 2 with 2,4,6-Trimethylbenzotrile Oxide.—The ketene acetal 2 (0.4 g, 2.47 mmol) and 2,4,6-trimethylbenzotrile oxide (0.4 g, 2.47 mmol) when irradiated at 450 W for 5 min (final temp. 96 °C) gave a mixture of two isomer cycloadducts (0.571 g, 72%) in a ratio of 3:2.

Major isomer: colourless oil (Found: C, 74.1; H, 6.2; N, 4.3. Calc. for C₂₀H₂₁NO₃: C, 74.3; H, 6.5; N, 4.3%); δ_{H} (200 MHz; CDCl₃) 2.28 (6 H, s, *ortho*-CH₃), 2.30 (3 H, s, *para*-CH₃), 3.42 (2 H, s, 4-H), 3.97 (1 H, dd, *J* 7.8 and 6.9, 5'a-H), 4.59 (1 H, dd, *J* 7.8 and 6.9, 5'b-H), 5.47 (1 H, t, *J* 6.9, 4'-H) and 6.90–7.44 (7 H, m, ArH); δ_{C} (75 MHz; CDCl₃) 19.63 (*ortho*-CH₃), 21.04 (*para*-CH₃), 42.7 (C-4), 71.7 (C-5'), 80.12 (C-4') and 126.83–159.14 (C-3, -5 and C-arom).

Minor isomer: m.p. 93–94 °C (Found: C, 74.15; H, 6.25; N, 4.3. Calc. for C₂₀H₂₁NO₃: C, 74.3; H, 6.5; N, 4.3%); ν_{\max} (KBr)/cm⁻¹ 3012 (=C–H), 1737 (C=N), 1608 (C=C), 1348 (N–O) and 1040 (C–O); δ_{H} (200 MHz; CDCl₃) 2.28 (6 H, s, *ortho*-CH₃), 2.29 (3 H, s, *para*-CH₃), 3.25 (1 H, d, *J* 16.7, 4a-H), 3.45 (1 H, d, *J* 16.7, 4b-H), 4.06 (1 H, dd, *J* 9.7 and 8.5, 5'a-H), 4.47 (1 H, dd, *J* 8.5 and 6.5, 5'b-H), 5.21 (1 H, dd, *J* 9.7 and 6.5, 4'-H) and 6.90–7.57 (7 H, m, ArH); δ_{C} (75 MHz; CDCl₃) 19.62 (*ortho*-CH₃), 19.92 (*para*-CH₃), 42.54 (C-4), 71.84 (C-5'), 78.08 (C-4') and 126.04–158.99 (C-3, -5 and C-arom).

Hetero-Diels–Alder Cycloaddition of the Ketene Acetal 2 with Methyl Vinyl Ketone.—The ketene acetal 2 (0.2 g, 1.23 mmol) and methyl vinyl ketone (0.086 g, 1.23 mmol) when irradiated at 780 W for 10 min (final temp. 95 °C) gave a mixture of two isomeric cycloadducts (0.246 g, 86%) in a ratio of 7:2 as a colourless oil (Found: C, 72.2; H, 6.9. Calc. for C₁₄H₁₆O₃: C, 72.4; H, 6.95%); ν_{\max} (KBr)/cm⁻¹ 3020 (=C–H) and 1028 (C–O).

Major isomer: δ_{H} (200 MHz; CDCl₃) 1.79 (3 H, s, CH₃), 2.07 (2 H, dd, *J* 12.4 and 6.4, 5-H), 2.24 (2 H, m, 4-H), 3.90 (1 H, dd, *J* 7.4 and 6.8, 5'a-H), 4.57 (1 H, t, *J* 7.4, 5'b-H), 4.60 (1 H, m, 3-H), 5.44 (1 H, t, *J* 6.8, 4'-H) and 7.31–7.38 (5 H, m, ArH).

Minor isomer: δ_{H} (200 MHz; CDCl₃) 1.78 (3 H, s, CH₃), 2.01 (2 H, dd, *J* 12.2 and 6.4, 5-H), 2.24 (2 H, m, 4-H), 4.06 (1 H, dd, *J* 9.6 and 8.2, 5'a-H), 4.42 (1 H, dd, *J* 8.2 and 6.6, 5'b-H), 4.60 (1 H, m, 3-H), 5.19 (1 H, dd, *J* 9.6 and 6.6, 4'-H) and 7.31–7.38 (5 H, m, ArH).

1,3-Dipolar Cycloaddition of the Ketene Acetal 3 with N-(Benzylidene)phenylamine N-Oxide.—The ketene acetal 3 (0.225 g, 2 mmol) and N-(benzylidene)phenylamine N-oxide (0.39 g, 2 mmol) when irradiated at 780 W for 10 min (final temp. 157 °C) gave a mixture of two isomeric cycloadducts, 14 and 15 (0.54 g, 88%) in a ratio of 9:2, respectively, as a colourless

oil (Found: C, 73.3; H, 6.7; N, 4.5. Calc. for $C_{19}H_{21}NO_3$: C, 73.3; H, 6.75; N, 4.5%).

Compound **14**: δ_H (300 MHz; $CDCl_3$) 1.17 and 1.19 (6 H, $2 \times d$, J 6.4, 4'- and 5'- CH_3), 2.70 (1 H, dd, J 13.2 and 9.0, 4a-H), 2.88 (1 H, dd, J 13.2 and 8.0, 4b-H), 4.54 (2 H, m, 4'- and 5'-H), 4.67 (1 H, t, J 9.0 and 8.0, 3-H), 6.93 (2 H, m, *ortho*-H 2-Ph), 7.49 (2 H, m, *ortho*-H 3-Ph) and 6.89–7.38 (6 H, m, other ArH).

Compound **15**: δ_H (300 MHz; $CDCl_3$) 1.34 and 1.35 (6 H, $2 \times d$, J 6.2, 4'- and 5'- CH_3), 2.65 (1 H, dd, J 12.9 and 9.2, 4a-H), 2.81 (1 H, dd, J 12.9 and 7.5, 4b-H), 4.34 (2 H, m, 4'- and 5'-H), 4.66 (1 H, dd, J 9.2 and 7.5, 3-H), 6.97 (2 H, m, *ortho*-H 2-Ph), 7.49 (2 H, m, *ortho*-H 3-Ph) and 6.89–7.38 (6 H, m, other ArH).

Hetero-Diels–Alder Cycloaddition of the Ketene Acetal 3 with Chalcone.—The ketene acetal **3** (0.166 g, 1.46 mmol) and chalcone (0.3 g, 1.46 mmol) when irradiated at 780 W for 10 min (final temp. 110 °C) gave compound **16** (0.34 g, 73%); eluent: toluene; m.p. 89–91 °C (Found: C, 78.15; H, 6.95. Calc. for $C_{21}H_{22}O_3$: C, 78.25; H, 6.9%; $\nu_{max}(KBr)/cm^{-1}$ 3023 (=C–H), 1596 (C=C) and 1018 (C–O); δ_H (300 MHz; $[^2H_6]DMSO$) 1.15 and 1.20 (6 H, $2 \times d$, J 6.5, 4'- and 5'- CH_3), 2.07 (1 H, t, J 12.2, 5a-H), 2.18 (1 H, dd, J 12.2 and 6.6, 5b-H), 3.89 (1 H, ddd, J 12.2, 6.6 and 2.2, 4-H), 4.60 and 4.71 (2 H, $2 \times m$, 4'- and 5'-H), 5.52 (1 H, d, J 2.2, 3-H), 7.36 (2 H, m, *ortho*-H 4-Ph), 7.61 (2 H, m, *ortho*-H 2-Ph) and 7.21–7.41 (6 H, m, other ArH).

1,3-Dipolar Cycloaddition of the Ketene Acetal 4 with N-(Benzyldiene)phenylamine N-Oxide.—The ketene acetal **4** (0.40 g, 1.68 mmol) and *N*-(benzyldiene)phenylamine *N*-oxide (0.33 g, 1.68 mmol) when irradiated at 780 W for 10 min (final temp. 150 °C) gave the cycloadduct **17** (0.695 g, 95%), m.p. 154–155 °C (Found: C, 79.85; H, 5.85; N, 3.15. Calc. for $C_{29}H_{25}NO_3$: C, 80.0; H, 5.75; N, 3.2%; $\nu_{max}(KBr)/cm^{-1}$ 3034 (=C–H), 1598 (C=C) and 1046 (C–O); δ_H (300 MHz; $CDCl_3$) 3.12 (1 H, dd, J 13.2 and 8.6, 4a-H), 3.37 (1 H, dd, J 13.2 and 8.0, 4b-H), 4.83 (1 H, t, J 8.6 and 8.3, 3-H), 5.76 and 5.79 (2 H, $2 \times d$, J 7.2, 4'- and 5'-H), 6.94 (4 H, m, *ortho*-H 4'- and 5'-Ph), 7.07 (2 H, m, *ortho*-H 2-Ph), 7.19 (2 H, m, *meta*-H 2-Ph), 7.32 (1 H, m, *para*-H 3-Ph), 7.39 (2 H, m, *meta*-H 3-Ph), 7.57 (2 H, m, *ortho*-H 3-Ph) and 6.93–7.07 (7 H, m, other ArH); δ_C (75 MHz; $CDCl_3$) 45.03 (C-4), 70.67 (C-3), 81.70 and 82.02 (C-4' and -5'), 126.22, 135.96, 136.08, 140.38 and 150.84 (C-5 and C-arom).

1,3-Dipolar Cycloaddition of the Ketene Acetal 4 with N-(4-Trifluorobenzylidene)phenylamine N-Oxide.—The ketene acetal **4** (0.1 g, 0.42 mmol) and *N*-(4-trifluorobenzylidene)phenylamine *N*-oxide¹⁰ (0.102 g, 0.42 mmol) when irradiated at 780 W for 10 min (final temp. 100 °C) gave compound **18** (0.16 g, 79%), m.p. 162–163 °C (Found: C, 72.7; H, 5.1; N, 5.8. Calc. for $C_{29}H_{24}N_2O_5$: C, 72.5; H, 5.0; N, 5.8%; $\nu_{max}(KBr)/cm^{-1}$ 3034 (=C–H), 1597 (C=C), 1523 (C–NO₂) and 1047 (C–O); δ_H (300 MHz; $CDCl_3$) 3.04 (1 H, dd, J 13.5 and 7.9, 4a-H), 3.44 (1 H, dd, J 13.5 and 8.3, 4b-H), 4.99 (1 H, t, J 8.3 and 7.9, 3-H), 5.76 (2 H, s, 4'- and 5'-H), 6.89–7.21 (15 H, m, ArH 2-, 4'- and 5'-Ph), 7.77 (2 H, m, *ortho*-H 3-Ph) and 8.25 (2 H, m, *meta*-H 3-Ph); δ_C (75 MHz; $CDCl_3$) 44.17 (C-4), 69.58 (C-3), 81.65 and 82.15 (C-4' and -5') and 116.41–150.22 (C-5 and C-arom).

Hetero-Diels–Alder Cycloaddition of the Ketene Acetal 4 with Methyl Vinyl Ketone.—The ketene acetal **4** (0.273 g, 1.14 mmol) and methyl vinyl ketone (0.08 g, 1.14 mmol) when irradiated at 780 W for 10 min (final temp. 100 °C) gave compound **19** (0.24 g, 69%), m.p. 90–91 °C (Found: C, 78.05; H, 6.5. Calc. for $C_{20}H_{20}O_3$: C, 77.9; H, 6.55%; $\nu_{max}(KBr)/cm^{-1}$ 3064 (=C–H),

1690 (C=C) and 1096 and 1026 (C–O); δ_H (200 MHz; $CDCl_3$) 1.83 (3 H, s, CH_3), 2.33 (4 H, m, 4- and 5-H), 4.64 (1 H, m, 3-H), 5.79 (2 H, s, 4'- and 5'-H) and 6.93–7.06 (10 H, m, ArH); δ_C (75 MHz; $CDCl_3$) 19.78, 19.94 and 28.29 (C-4, -5 and CH_3), 81.46 (C-3), 95.68 (C-4' and -5') and 118.93–148.88 (C-2, -5 and C-arom).

Hetero-Diels–Alder Cycloaddition of the Ketene Acetal 4 with Chalcone.—The ketene acetal **4** (0.46 g, 1.93 mmol) and chalcone (0.38 g, 1.93 mmol) when irradiated at 780 W for 10 min (final temp. 155 °C) gave the cycloadduct **20** (0.78 g, 91%); eluent: toluene; m.p. 110–111 °C (Found: C, 83.25; H, 5.8. Calc. for $C_{31}H_{26}O_3$: C, 83.4; H, 5.8%; $\nu_{max}(KBr)/cm^{-1}$ 3026 (=C–H), 1649 (C=C) and 1013 (C–O); δ_H (300 MHz; $CDCl_3$) 2.52 (1 H, t, J 12.9 and 12.2, 5a-H), 2.75 (1 H, ddd, J 12.9, 6.3 and 1.2, 5b-H), 4.14 (1 H, ddd, J 12.2, 6.3 and 2.3, 4-H), 5.55 (1 H, m, 3-H), 5.87 and 5.97 (2 H, $2 \times d$, J 7.6, 4'- and 5'-H), 6.99 and 7.02 (4 H, m, *ortho*-H 4'- and 5'-Ph), 7.42 (2 H, m, *ortho*-H 4-Ph), 7.68 (2 H, m, *ortho*-H 2-Ph) and 6.98–7.42 (12 H, m, other ArH); δ_C (75 MHz; $CDCl_3$) 37.38 (C-5), 38.76 (C-4), 81.39 and 82.15 (C-4' and -5'), 101.75 (C-3), 119.66 (C-2) and 124.79–170.58 (C-6 and C-arom).

Acknowledgements

Financial support from Spanish CICYT (PB91-0310) and a grant (P. P.) (Junta de Comunidades de Castilla-La Mancha) are gratefully acknowledged. Technical assistance from Mrs. Esther Vazquez is also acknowledged.

References

- W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, Pergamon Press, Oxford, 1990.
- A. Diaz-Ortiz, E. Diez-Barra, A. de la Hoz and P. Prieto, *Synth. Commun.*, 1993, **23**, 1935.
- For example: (a) R. Huisgen, R. Grashey, H. Seild and H. Hauck, *Chem. Ber.*, 1968, **101**, 2559; (b) D. Keirs, D. Moffat, K. Overton and R. Tomanek, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1041.
- For example: (a) A. Bérlanger and P. Brassard, *J. Chem. Soc., Chem. Commun.*, 1972, 863; (b) G. H. Posner and W. Harrison, *J. Chem. Soc., Chem. Commun.*, 1985, 1785; (c) U. Gruseck and M. Heuschmann, *Chem. Ber.*, 1990, **123**, 1905.
- (a) R. A. Abramovitch, *Org. Prep. Proc. Int.*, 1991, **23**, 685; (b) D. M. P. Mingos and D. R. Barghurst, *Chem. Soc. Rev.*, 1991, **20**, 1.
- A. Loupy, A. Petit, M. Ramdani, C. Yvanaeff, M. Majdoub, B. Labiad and D. Villemin, *Can. J. Chem.*, 1993, **71**, 90.
- (a) R. J. Giguere, T. L. Bray, S. M. Duncan and G. Majetich, *Tetrahedron Lett.*, 1986, **27**, 4945; (b) J. Berlan, P. Giboreau, S. Lefevre and C. Marchand, *Tetrahedron Lett.*, 1991, **32**, 2363; (c) R. N. Geyde, W. Rank and K. C. Westaway, *Can. J. Chem.*, 1991, **69**, 706; (d) A. Stambouli, M. Chastrette and M. Soufiaoui, *Tetrahedron Lett.*, 1991, **32**, 1723; (e) S. S. Bari, A. K. Bose, A. G. Chaudhary, M. S. Manhas, V. S. Raju and E. W. Robb, *J. Chem. Ed.*, 1992, **69**, 938; (f) K. D. Raner, C. R. Strauss, F. Vyskoc and L. Mokbel, *J. Org. Chem.*, 1993, **58**, 950.
- (a) A. Diaz-Ortiz, E. Diez-Barra, A. de la Hoz, A. Loupy, A. Petit and L. Sánchez, *Heterocycles*, 1994, **38**, 785; (b) B. Touaux, B. Klein, F. Texier-Boulet and J. Hamelin, *J. Chem. Res.*, 1994, (S), 116.
- (a) A. K. Bose, M. S. Manhas, M. Ghosh, M. Shah, V. S. Raju, S. S. Bari, S. N. Newaz, B. K. Banik, A. G. Chaudhary and K. J. Barakat, *J. Org. Chem.*, 1991, **56**, 6968; (b) F. Texier-Boulet, R. Latouche and J. Hamelin, *Tetrahedron Lett.*, 1993, **34**, 2123.
- T. Brüning, R. Grashey, H. Hauck, R. Huisgen and H. Seild, *Org. Synth.*, 1973, **5**, 1124.
- C. Grundmann and R. Richter, *J. Org. Chem.*, 1968, **33**, 476.

Paper 4/04773G

Received 3rd August 1994

Accepted 2nd September 1994