

# Reactivity of ethyldiazoacetate towards alkenes under microwave irradiation<sup>†</sup>

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Ethyldiazoacetate reacts with alkenes as 1,3 -dipole or as carbene precursor according to the reaction conditions. Comparison with literature reports shows that microwave irradiation can accelerate the process and even enhance the yields in some cases.

**Keywords:** ethyldiazoacetate, alkenes

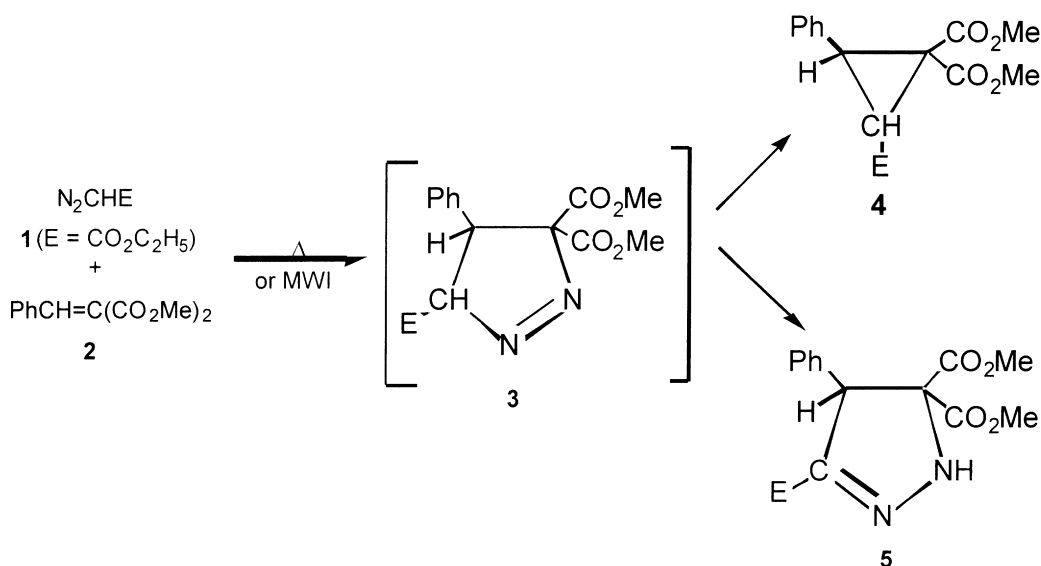
During the last 30 years, 1,3-dipolar cycloadditions have proved to be an excellent tool for heterocycles synthesis.<sup>1–4</sup> Recently, 1,3-dipolar cycloadditions under microwave irradiation have been reported for nitrones, pyridinium ylides, nitrilimine and nitrile oxides.<sup>5</sup> As far as we know, the reactivity of diazocompounds under microwave irradiation (MWI) has not been reported previously.

As a model reaction for 1,3-dipolar cycloadditions we have studied the addition of ethyldiazoacetate (EDA) **1** to methyl benzylidene malonate **2**. This reaction has already been studied<sup>6</sup> under classical conditions and leads, via the unstable 1-pyrazoline **3**, to the cyclopropane **4**. The 2-pyrazoline **5** is not observed (Scheme 1). When **1** and **2** in equimolar amounts were refluxed in toluene for 12 days, only 33% of **2** was transformed in 33% of cyclopropane **4** and the complete transformation of the alkene needed 39 days and 500% excess of EDA.

In the latter conditions the irradiation at 150 Watts (115°C) in a focused microwave oven (Synthewave 402<sup>®7</sup>) leads to the transformation of 69% of the alkene **2** in 46 % of pyrazoline **5** and 23% of cyclopropane **4**, after six hours (sequential irradiation).

Under microwave irradiation the reaction is much faster and allows the formation of the 2-pyrazoline **5**, which is not observed under classical conditions. This may be due to the modification of the relative rates under irradiation. Nevertheless owing to the very long irradiation times we did not continue with these conditions. It has been shown previously<sup>6</sup> that under classical heating without solvent, the mixture of **1** (25% excess) and **2** leads, after 10 days at 50°C, to the 2-pyrazoline **5** in 92% yield. So we decided to study the reaction without solvent under microwave irradiation using equimolar amounts of **1** and **2**. The results of the various experiments are reported in Table 1.

Up to 100 Watts, the formation of the 2-pyrazoline **5** is exclusive. When the irradiation power is raised, the cyclopropane **4** appears and the yield goes up to 27% at a power of 150 Watts, and this remains the limit even at higher power. The formation of the cyclopropane at higher power is not the result of the addition of the carbene because we have shown that EDA alone was not decomposed in the same conditions, and it is known that the electron poor carbenes do not react with electron poor alkenes. The primary 1-pyrazoline **3** was



Scheme 1

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<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

**Table 1** Addition of EDA to benzylidene malonate under microwave irradiation

Power/W	Time/min	Starting materials/%	4%	5%
30	180	73	–	27
60	180	22	–	78
100	30	18	–	82
100	60	14	–	86
120	30	15	15	70
120	60	12	15	73
150	5	36	20	44
150	15	25	22	53
150	30	16	27	57

never evident in these experiments, and it may be assumed that a low power (low temperature) isomerises **3** into the 2-pyrazoline **5**, and at higher temperature the decomposition to cyclopropane **4** competes.

These results show that 1,3-dipolar cycloaddition of EDA is readily achieved under microwave irradiation without solvent leading to 86% yield of **5** after one hour at 100 W instead of 92% in 10 days at 50°C under conventional heating.


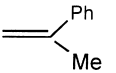
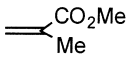

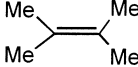
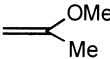



We were also interested in the cyclopropanation of alkenes with EDA by metal catalysed reactions. This type of reaction is well documented,<sup>8,9</sup> and some recent reports show that the experimental conditions can affect the diastereoselectivity of the reaction.<sup>10</sup> Our continuous interest in microwave-assisted reactions<sup>5</sup> led us to investigate the cyclopropanation with EDA in the presence of catalytic amounts of  $\text{Cu}(\text{acac})_2$  under microwave irradiation.

Our first experiments were realised without solvent using an equimolar amount of cyclohexene and EDA with 2% of  $\text{Cu}(\text{acac})_2$ . Even at low irradiation power, a very fast reaction occurs which produces only methyl maleate and fumarate, the former dimerisation products of the carbene. In order to overcome this drawback we studied the reaction in solution either in toluene or in the alkene as solvent. The Synthewave 402<sup>®</sup> fitted with a refluxing condenser is suitable for this study. In these conditions (see experimental section) EDA reacted with a variety of alkenes to give a mixture of the corresponding diastereomeric cyclopropanes in good yields (Scheme 2, Table 2).

This procedure results in a small yield of dimerisation products (ethyl maleate or fumarate < 10%), by keeping the concentration of ethyl diazoacetate low, either in toluene or in excess of alkene as solvent (entries **4** and **7**).

In several cases, the investigated reactions were shown to proceed with major *trans* stereochemistry. This observation agrees with the formation of the thermodynamically more stable isomer. Stereoselectivities depend on the olefinic system. With styrene and gem-disubstituted alkenes the ratio of *E/Z* isomers varied from 76/24 to 50/50, however, with cyclic alkenes the diastereoselectivity was highly increased and diastereomer ratios between 90/10 and 100 were obtained. The structures of the cyclopropanes were assigned on the basis of their  $^1\text{H}$  NMR spectra, and in comparison with the literature data.

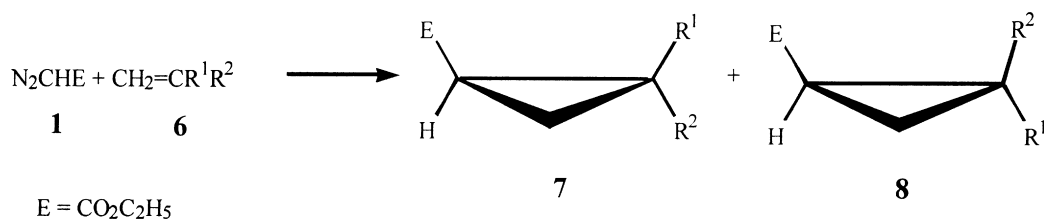
**Table 2** Cyclopropanation of various alkenes under microwave irradiation and classical heating

Entry	Alkenes	MWI			$\Delta^e$	
		%7 <sup>a</sup>	%8 <sup>a</sup>	Yield <sup>b</sup> /%	%7 <sup>a</sup>	%8 <sup>a</sup>
1		75	25	94	75	25
2		70	30	80	63	37
3		68	32	25 <sup>c</sup>	50	50
4	//	66	34	<sup>d</sup>	50	50
5		100		85	100	
6		100		31 <sup>c</sup>	100	
7	//	100		<sup>d</sup>		
8		50	50	80		
9		90	10	87	90	10
10		100		75	100	
11		92	8	88	100	

<sup>a</sup>Estimated by <sup>1</sup>H NMR. <sup>b</sup>Yields of isolated products based on EDA. <sup>c</sup>Competitive reactions with toluene were observed (entries **3** and **6**). <sup>d</sup>Reactions were performed in alkene as solvent, and only **7** appeared in small amounts in the NMR spectra of the crude product and, owing to the great deal of polymerisation, the product was not isolated. <sup>e</sup>As this study was done only for comparison, the products were not isolated and the ratio were estimated by <sup>1</sup>H NMR.

In the entries **3** and **6** the diazo compound reacts with toluene giving a complex mixture in which two cycloheptatrienyl esters were characterised. Toluene and EDA are known to produce ring-expanded products.<sup>11</sup>

When the alkene was used as solvent, polymerisation of the substrate was a side reaction of the cyclopropanation (entries **7** and **10**), and yields of the desired cyclopropanes were low. Similar observations are reported in the literature<sup>12</sup> in classical conditions.



### Scheme 2

We compared the results of the present synthesis using microwaves with classical heating. It can be seen from Table 2 that results obtained under classical heating are not significantly different. Diastereoselectivity of the cyclopropanation is essentially unaffected, and the amount of dimerisation products (diethyl fumarate and maleate) may be highly reduced under microwave irradiation.

In conclusion microwave irradiation accelerates the process of 1,3-dipolar cycloadditions, while cyclopropanation rate and the diastereoselectivity were essentially unaffected as compared with classical heating.

## Experimental section

NMR spectra were measured on a Bruker FT AM 200 Spectrometer using  $\text{CDCl}_3$  as solvent and TMS as internal standard ( $\delta$  in ppm,  $J$  in Hz). High-resolution mass spectrometry (EI) was performed at the Centre de Mesures Physiques de l'Ouest, Rennes on a Varian MAT 311 spectrometer.

**General Procedure for the preparation of cyclopropanes: Method A (MWI):** The mixture of the alkene (8 mmol, 4 eq) and the catalyst (0.04 mmol, 2% with respect to EDA) in toluene (10 ml) was irradiated at 300 Watts to reach  $110^\circ\text{C}$ , in a quartz reactor ( $\phi = 4$  cm). The reflux was maintained for 20 minutes and during that time, EDA (2 mmol, 1 eq) in toluene (10 ml) was added dropwise. The suspension was filtered through a plug of celite or silica gel, which was washed with  $\text{CH}_2\text{Cl}_2$ . After evaporation of the solvent, the resulting mixture of diastereoisomers was analysed by  $^1\text{H}$  NMR. When the alkene was used as solvent, 2 eq were mixed with the catalyst and EDA was dissolved in 2 eq of alkene for dropwise addition during irradiation. For cycloaddition reactions, alkenes and EDA were allowed to react without solvent (time and power of irradiation are given in Table 1).

**Method B (conventional heating):** Reactions were performed in an oil bath previously set at the temperature measured in the microwave oven. As this study was done only for comparison, the products were not isolated and the ratio were determined by  $^1\text{H}$  NMR.

**3-Phenyl-cyclopropane-1,2-dicarboxylic acid 2-ethyl ester 1-methyl ester<sup>6</sup>:**  $^1\text{H}$  NMR:  $\delta = 1.30$  (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ ); 3.23 (1H, d,  $^3J_{\text{HH}} = 8$ ); 3.63 (1H, d,  $^3J_{\text{HH}} = 8$ ); 3.48 (3H, s,  $\text{CO}_2\text{CH}_3$ ); 3.81 (3H, s,  $\text{CO}_2\text{CH}_3$ ); 4.19 (2H, m,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ); 7.10–7.50 (5H, m, Ar-H).

**4-Phenyl-2,4-dihydro-pyrazole-3,3,5-tricarboxylic acid 5-ethyl ester 3,3-dimethyl ester<sup>6</sup>:**  $^1\text{H}$  NMR:  $\delta = 1.18$  (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ); 3.19 (3H, s,  $\text{CO}_2\text{CH}_3$ ); 3.84 (3H, s,  $\text{CO}_2\text{CH}_3$ ); 4.19 (2H, m,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ); 5.27 (1H, s,  $\text{CHPh}$ ); 7.1–7.5 (5H, m, Ar-H).

**2-Phenyl-cyclopropanecarboxylic acid ethyl ester<sup>13</sup>:** Yield: 94%; Liquid; b.p.,  $137$ – $143^\circ\text{C}$ .  $^1\text{H}$  NMR:  $\delta = 0.95$  (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ ); 1.25 (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ ); 1.5–2.6 (4H, m, E+Z); 3.85 (2H, q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ ); 4.16 (2H, q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ ); 7.00–7.35 (5H, m, Ar-H).  $^{13}\text{C}$  NMR:  $\delta = 11.07$  ( $\text{CH}_2$ , t,  $^1J_{\text{CH}} = 160.02$ ); 14.01 ( $\text{CO}_2\text{CH}_2\text{CH}_3$ , q,  $^1J_{\text{CH}} = 126.9$ ); 14.20 (q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.9$ ); 17.05 ( $\text{CH}_2$ , t,  $^1J_{\text{CH}} = 165.4$ ); 21.79 (d,  $\text{CHCO}_2\text{Et}$ ,  $^1J_{\text{CH}} = 167.2$ ); 24.19 (d,  $\text{CHCO}_2\text{Et}$ ,  $^1J_{\text{CH}} = 165.4$ ); 25.45 (d,  $\text{CHPh}$ ,  $^1J_{\text{CH}} = 165.2$ ); 26.16 (d,  $\text{CHPh}$ ,  $^1J_{\text{CH}} = 165.2$ ); 60.66 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 147.4$ ); 61.18 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 147.4$ ); 128–140 (Ar); 170.89 (s,  $\text{CO}_2\text{Et}$ , Z); 173.33 (s,  $\text{CO}_2\text{Et}$ , E); HRMS:  $\text{C}_{12}\text{H}_{14}\text{O}_2$ . Calc = 190.099; Fd = 190.099.

**2-Methyl-2-phenyl-cyclopropanecarboxylic acid ethyl ester<sup>14</sup>:** Yield: 80%; Liquid; b.p.,  $114$ – $116^\circ\text{C}/5\text{mm Hg}$ .  $^1\text{H}$  NMR:  $\delta = 0.92$  (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J = 7.1$ , Z); 1.12–1.21 (4H, m, E+Z); 1.31 (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J = 7.1$ , E); 1.52 (3H, s,  $\text{CH}_3$ , Z); 1.8–2.1 (2H, m, E+Z); 3.80 (2H, q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J = 7.1$ , Z); 4.16 (2H, q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J = 7.1$ , E); 7.12–7.24 (10H, m).  $^{13}\text{C}$  NMR:  $\delta = 13.95$  (t,  $\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.86$  Z); 14.40 (t,  $\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.86$ , E); 19.35 (q,  $\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.81$ , Z); 19.83 (q,  $\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.81$ , E); 20.74 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 160.91$ , Z); 27.83 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 155.92$ , E); 28.50 (d,  $\text{CHCO}_2\text{Et}$ ,  $^1J_{\text{CH}} = 166.4$ , Z); 28.72 (d,  $\text{CHCO}_2\text{Et}$ ,  $^1J_{\text{CH}} = 164.15$ , E); 30.51 (s,  $\text{CPhMe}$ , Z); 31.96 (s,  $\text{CPhMe}$ , E); 59.97 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 147.09$ , Z); 61.41 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 147.40$ , E); 125.42–145.85 (arom); 171.06 (s,  $\text{CO}_2\text{Et}$ , Z); 172.02 (s,  $\text{CO}_2\text{Et}$ , E). HRMS:  $\text{C}_{13}\text{H}_{16}\text{O}_2$ . Calc = 204.114; Fd = 204.115.

**Cyclopropane-1,2-dicarboxylic acid 2-ethyl ester 1-methyl ester<sup>15</sup>:** Yield: 70%; Liquid; b.p.,  $120$ – $130^\circ\text{C}/15\text{mm Hg}$ .  $^1\text{H}$  NMR:  $\delta = 1.24$  (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ , E); 1.27 (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ , Z); 1.39 (6H,  $\text{CH}_3$ , s); 1.3–1.8 (4H, m), 2.32 (2H, dd,  $^3J = 6.64$ ), 3.67 (3H, s,  $\text{CO}_2\text{CH}_3$ ); 3.69 (3H, s,  $\text{CO}_2\text{CH}_3$ ); 4.13 (4H, m,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR:  $\delta = 12.83$  (q,  $\text{CH}_3$ ,  $^1J_{\text{CH}} = 129.34$ , Z); 14 (q,  $\text{CH}_3$ ,  $^1J_{\text{CH}} = 123.96$ , E); 14.11 (q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.29$ , Z); 19.37 (t,  $\text{CH}_2$ ,

$^1J_{\text{CH}} = 165.23$ , Z); 20.77 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 165.56$ , E); 20.88 (q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.88$ , E); 26.65 (s,  $\text{CCH}_3\text{CO}_2\text{Me}$ , Z); 27.72 (d,  $\text{CHCO}_2\text{Et}$ ,  $^1J_{\text{CH}} = 165.59$ , Z); 28.58 (d,  $\text{CHCO}_2\text{Et}$ ,  $^1J_{\text{CH}} = 166.6$ , E); 28.67 (s,  $\text{CCH}_3\text{CO}_2\text{CH}_3$ , E); 51.93 (q,  $\text{CO}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 147.02$ , Z); 52.19 (q,  $\text{CO}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 147.14$ , E); 60.64 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 147.45$ , Z); 60.72 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 147.45$ , E); 170.12 (s,  $\text{CO}_2\text{Et}$ , Z); 170.28 (s,  $\text{CO}_2\text{Et}$ , Z); 171.88 (s,  $\text{CO}_2\text{Me}$ , Z); 173.75 (s,  $\text{CO}_2\text{Me}$ , E). HRMS:  $\text{C}_9\text{H}_{14}\text{O}_4$ . Calc = 186.087; Fd = 186.089.

**2-Ethanoxy-oxy-cyclopropanecarboxylic acid ethyl ester<sup>16</sup>:** Yield: 85%; Liquid; b.p.,  $95^\circ\text{C}/10\text{mm Hg}$ .  $^1\text{H}$  NMR:  $\delta = 1.25$  (3H, t,  $\text{CH}_2\text{CH}_3$ );  $^3J_{\text{HH}} = 7.1$ ; 1.36–1.59 (2H, m,  $\text{CH}_2$ ); 1.84–2.00 (1H, m,  $\text{CHCO}_2\text{Et}$ ); 2.05 (3H s,  $\text{COCH}_3$ ); 4.14 (2H, q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ ); 4.40 (1H, m,  $\text{CHCOMe}$ ).  $^{13}\text{C}$  NMR:  $\delta = 11.92$  (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 168$ ); 13.87 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 165.48$ ); 14.03 (q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.98$ ); 19.73 (d,  $\text{CHCO}_2\text{Et}$ ,  $^1J_{\text{CH}} = 170.37$ ); 20.42 (q,  $\text{COCH}_3$ ,  $^1J_{\text{CH}} = 129.73$ ); 52.49 (d,  $\text{CHCOMe}$ ,  $^1J_{\text{CH}} = 195.45$ ); 60.63 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 147.47$ ); 169.33 (s,  $\text{COMe}$ ); 171.25 (s,  $\text{CO}_2\text{Et}$ ); 171.44. HRMS: No moléculaire ion ( $m/z = 172$ ), observation of  $m/z = 130$  ( $\text{M}^+ - \text{CH}_2 = \text{C} = \text{O}$ );  $m/z = 143$  ( $\text{M}^+ - \text{C}_2\text{H}_5$ ).

**2,3-tetramethyl-cyclopropanecarboxylic acid ethyl ester<sup>17</sup>:** Yield: 31%; Liquid; b.p.,  $71$ – $73^\circ\text{C}/12\text{mm Hg}$ .  $^1\text{H}$  NMR:  $\delta = 1.18$  (3H, s); 1.24 (3H, s); 1.25 (1H, s); 1.31 (3H, t,  $^3J_{\text{HH}} = 7.1$ ); 4.07 (2H, q,  $^3J_{\text{HH}} = 7.1\text{Hz}$ ).  $^{13}\text{C}$  NMR:  $\delta = 16.47$  (q,  $\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.40$ ); 23.46 (q,  $\text{CH}_3$ ,  $^1J_{\text{CH}} = 125.73$ ); 29.79 (s, Cq); 35.96 (d,  $\text{CH}$ ,  $^1J_{\text{CH}} = 159.55$ ); 59.45 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 146.76$ ); 172.09 (s,  $\text{CO}_2\text{Et}$ ). HRMS:  $\text{C}_{10}\text{H}_{18}\text{O}_2$ . Calc = 170.1306; Fd = 170.1308.

**Bicyclo [4.1.0] heptane-7-carboxylic acid ethyl ester<sup>18</sup>:** Yield: 87%; Liquid; b.p.,  $115^\circ\text{C}/12\text{mm Hg}$ .  $^1\text{H}$  NMR:  $\delta = 1.05$ – $1.98$  (11 H, m); 1.25 (3H, t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ ); 4.10 (2H, q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$ ).  $^{13}\text{C}$  NMR:  $\delta = 14.02$  (q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 126.9$ ); 20.90 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 130.8$ ); 21.97 (d,  $\text{CH}$ ,  $^1J_{\text{CH}} = 163.0$ ); 22.67 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 134.4$ ); 25.60 (d,  $\text{CH}$ ,  $^1J_{\text{CH}} = 172.0$ ); 61.11 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 147.0$ ); 174.73 (s,  $\text{CO}_2\text{Et}$ ). HRMS:  $\text{C}_{10}\text{H}_{16}\text{O}_4$ . Calc = 168.115; Fd = 168.114.

**Bicyclo [6.1.0] nonane-9-carboxylic acid ethyl ester<sup>19</sup>:** Yield: 75%; Liquid; b.p.,  $105^\circ\text{C}/1.5\text{ mm Hg}$ .  $^1\text{H}$  NMR:  $\delta = 1.09$  (m, 3H, ); 1.25 (3H, t,  $^3J_{\text{HH}} = 7.1$ ); 1.29–2.22 (3H, m); 4.09 (q, 2H,  $^3J_{\text{HH}} = 7.1$ ); 4.23 (m, 2H).  $^{13}\text{C}$  NMR:  $\delta = 14.20$  (q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 125$ ); 14.27 (q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 125.51$ ); 20.67 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 127.31$ ); 20.81 (d,  $\text{CH}$ ,  $^1J_{\text{CH}} = 161.17$ ); 24.47 (d,  $\text{CH}$ ,  $^1J_{\text{CH}} = 165.16$ ); 25.71 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 124.22$ ); 25.78 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 124.22$ ); 26.29 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 123.54$ ); 27.15 (d,  $\text{CHCO}_2\text{Et}$ ,  $^1J_{\text{CH}} = 160.33$ ); 29.10 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 124.55$ ); 29.10 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 124.55$ ); 59.55 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 146.67$ ); 60.06 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ,  $^1J_{\text{CH}} = 146.97$ ); 172.23 (s,  $\text{CO}_2\text{Et}$ ); 174.29 (s,  $\text{CO}_2\text{Et}$ ). HRMS:  $\text{C}_{12}\text{H}_{20}\text{O}_2$ . Calc = 196.144; Fd = 196.146.

**Tricyclo [3.2.1.0] octane-3-carboxylic acid ethyl ester<sup>20</sup>:** Yield: 88%; Liquid; b.p.,  $65^\circ\text{C}/0.8\text{ mm Hg}$ .  $^1\text{H}$  NMR:  $\delta = 0.6$ – $1.9$  (9H, m); 2.36 (2H, s); 2.51 (2H, d); 4.03–4.13 (q, 2H,  $\text{CO}_2\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR:  $\delta = 14.29$  (q,  $\text{CH}_3$ ,  $^1J_{\text{CH}} = 127$ ); 16.30 (d,  $\text{CH}$ ,  $^1J_{\text{CH}} = 149.1$ ); 25.94 (d,  $\text{CH}$ ,  $^1J_{\text{CH}} = 152.1$ ); 28.58 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 141.5$ ); 28.70 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 145.4$ ); 35.62 (d,  $\text{CH}$ ,  $^1J_{\text{CH}} = 143.5$ ); 60.20 (t,  $\text{CH}_2$ ,  $^1J_{\text{CH}} = 124$ ); 174.23 (s,  $\text{CO}_2\text{Et}$ ). HRMS:  $\text{C}_{11}\text{H}_{16}\text{O}_2$ . Calc = 180.115; Fd = 180.115.

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## References

- 1 R. Huisgen, *Angew. Chem. Intern. Ed.*, 1963, **10**, 565.
- 2 R. Huisgen, *Angew. Chem. Intern. Ed.*, 1963, **11**, 633.
- 3 (a) D.P. Curran, Ed., *Advances in cycloaddition*, Vol 1, JIA Press, 1988; (b) D.P. Curran, Ed., *Advances in cycloaddition*, Vol 2, JIA Press, 1990.
- 4 M. Regitz and H. Heydt, in *1,3-Dipolar Cycloaddition Chemistry* A. Padwa Ed., Vol 1, John Wiley & Sons, New York, 1984.
- 5 (a) H. Kaddar, J. Hamelin and H. Benhaoua, *J. Chem. Res. (S)*, 1999, 718 and references cited; (b) A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault and D. Mathé, *Synthesis*, 1998, **9**, 1213.
- 6 M. Le Coënt, Thèse de 3ème Cycle, Université de Rennes 1, 1968.
- 7 We used a focused microwave oven: Synthwave 402®. This oven is fitted with an open reactor vessel and a stirring device. R. Commarmot, R. Diderot, J.F. Gardais, Rhone-Poulenc/Prolabo, Patent Number 84/03496. October 27th 1986. The temperature is measured by an IR captor, Prolabo, Patent Number 62241D. 14669 FR. December 23rd 1991.
- 8 (a) G. Mass, *Top. Curr. Chem.*, 1987, **137**, 75; (b) T. Ye and T. M.A Mckerverey, *Chem. Rev.*, 1994, **94**, 1091; (c) A.F. Noels, A. Demonceau in *Applied Homogeneous Catalysis with*

- Organometallic Compounds*, Vol 2, Developments, B. Cornils and W.A. Hermann, Ed., VCH, 1996, 733; (d) M. Regitz and G. Mass, in '*Diazocompounds properties and Synthesis*' Academic press, Orlando 1986; (e) M. Brookhart and W.B. Studabaker, *Chem. Rev.*, 1987, **87**, 411.
- 9 (a) M.P. Doyle in *Comprehensive Organometallic Chemistry*, Vol. 12, Ed., Pergamon, New York 1995; (b) M.P. Doyle, *Chem. Rev.*, 1986, **86**, 919.
  - 10 (a) J. Pfeiffer, M. Nieger and K.H. Dotz, *Eur. J. Org. Chem.*, 1998, 1011; (b) M. Hagen and U. Lüning, *Chem. Ber. Recueil*, 1997, **130**, 231; (c) M.P. Doyle in *Catalytic Asymmetric Synthesis*, Ed., I. Ojima, VCH, New York, 1993, **63**; (d) M.P. Doyle, R.L. Dorow, J.H. Griffin, W.H. Tamblin and M.L. Trudell, *Organometallics*, 1984, **3**, 44.
  - 11 M.W. Majchrzak and A. Kotelko, *Synthesis*, 1983, 469.
  - 12 R. Paulissen, A.J. Hubert and P. Teyssié, *Tetrahedron Lett.*, 1972, 1465.
  - 13 M.P. Doyle, R.L. Dorow and W.H. Tamblin, *J. Org. Chem.*, 1982, **47**, 4059.
  - 14 K.B. Wiberg and R. Barnes, *J. Org. Chem.*, 1958, **23**, 299.
  - 15 (a) C.D. Paultier and S. Winstein, *J. Am. Chem. Soc.*, 1972, **94**, 2297; (b) A.P. Meshcheryakov and I.E. Dolgii, *Izv. Akad. Nauk. SSSR, Otd. Khim.*, 1960, 931.
  - 16 M.P. Doyle, D. Van Leusen and W.H. Tamblin, *Synthesis*, 1981, 787.
  - 17 A.J. Hubert, A.F. Noels, A.J. Anciaux and P. Teyssié, *Synthesis*, 1976, 600.
  - 18 R.P. Corbally, M.J. Perkins and P.A. Elnitski, *J. Chem. Soc., Perkin Trans. I*, 1979, 793.
  - 19 R.R. Sauers and P.E. Sonnet, *Tetrahedron*, 1964, **20**, 1029.
  - 20 K. Alder, R. Munders, W. Krane and P. Wirtz, *Liebigs Ann.Chem.*, 1959, **59**, 627.
  - 21 A. Demonceau, F. Simal, A.F. Noels, C. Viñas, R. Nuñez and F. Teixidor, *Tetrahedron Lett.*, 1997, **38**, 7879.