

First Intermolecular [2 + 2] Cycloaddition of Heterosubstituted Methyleneketenes to Chloral (Trichloroacetaldehyde)

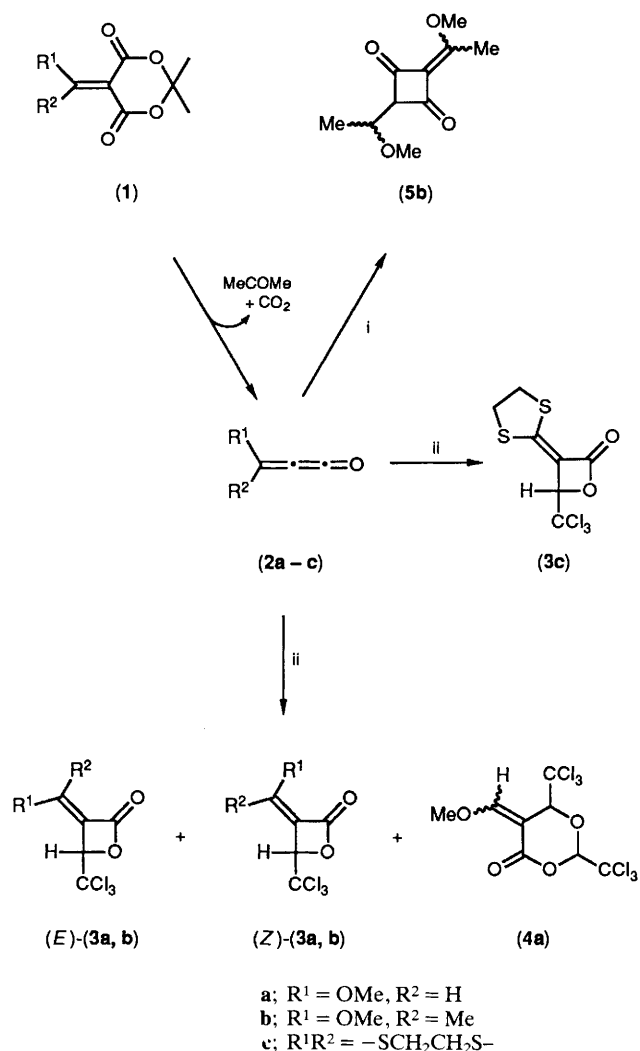
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Heterosubstituted methyleneketenes undergo intermolecular [2 + 2] cycloaddition to chloral leading to α -methylenepropiolactones.

In contrast to ketenes, the chemistry of methyleneketenes is still relatively undeveloped.¹ Recently, the synthetic utility of these compounds has been greatly improved by the discovery that aminomethyleneketenes, generated through the pyrolysis of Meldrum's acid derivatives, could be converted to a variety

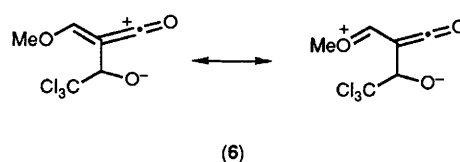
of azaheterocycles.²⁻⁵ Moreover, we have recently found that some heterosubstituted methyleneketenes⁶ are much more stable than their aryl and alkyl homologues.⁷ Whereas these later compounds are obtainable only as fleeting intermediates in the gas phase, methyleneketenes such as (2) can be handled



Scheme 1. Reagents and conditions: i, see ref. 6a; ii, CCl₃CHO, CH₂Cl₂.

in solution at low temperature. We have taken advantage of this increased stability to explore the intermolecular reactivity of these cumulenones. We report here the first [2 + 2] cycloaddition reactions involving methyleneketene (**2**) and chloral.

Cumulenones (**2a–c**), generated by flash vacuum pyrolysis of (**1a–c**) (temperature range 550–600 °C; 10⁻⁴ Torr), were received on a cold finger (-196 °C) covered with methylene chloride. After the end of the pyrolysis, the cold finger was allowed to warm and the resulting cold solution dripped into a stirred solution of chloral in methylene chloride, maintained at a temperature which depended on the stability of the cumulenone [(**1a**): -20; (**1b**): 0; (**1c**): -40 °C]. After one hour at this temperature and a further hour at room temperature, the solution was concentrated and the residue was purified by flash chromatography leading to a (*Z*)- and (*E*)-mixture of α -methylene propiolactones (**3a**) and (**3b**) starting respectively from (**1a**) and (**1b**) and the α -methylene propiolactone (**3c**) from (**1c**). A small amount (3% yield) of compound (**4a**) was also obtained from (**1a**) (Table 1). It is noteworthy that the known dimerization^{6a} of (**2b**) to (**5b**) was not observed.



Scheme 2

Table 1. Yields of isolated products.^a

Starting material	Temp./°C	% Yields of products		
		(3)	(<i>E/Z</i>) ^b	(4) ^c
(1a)	580	74	68/32	3
(1b)	550	81	63/37	—
(1c)	600	68	—	—

^a Yields are based on products isolated by flash chromatography on silica using pentane–ethyl acetate as eluant. ^b For (**3**). ^c *E/Z* 3/2.

New compounds were identified from spectral and analytical data.[†] The methylenelactones (**3**) give a strong IR absorption between 1800 and 1830 cm⁻¹, typical of β -propiolactones. Moreover, the C=C stretching frequencies for (*E*)-(**3a,b**) are *ca.* 30 cm⁻¹ higher than for (*Z*)-(**3a,b**). Supplementary evidence in favour of the (*E*)- or (*Z*)-stereochemistry was obtained from the ¹H NMR spectra: a deshielding of *ca.* 0.15–0.30 ppm was observed for the methoxy protons of the (*Z*)-derivatives (**3a,b**) which are close to the carbonyl group.

The minor product (**4a**) is a mixture of two isomers which were separated by TLC (*E/Z*: 3/2). The arguments in favour of the (*E*)- or (*Z*)-stereochemistry are also based on the relative chemical shifts of the methoxy and ethylenic protons of the methylene group. Only a small increase in the yield of (**4a**) was found with an excess of chloral (6% with a six-fold excess of chloral). We did not detect any trace of the homologues (**4b, c**).

At present, it is not possible to know whether the formation of the four-membered ring is a result of a concerted or a stepwise [2 + 2] cycloaddition. However, the isolation of the 1:2 adduct (**4a**) is best interpreted as resulting from a 1,4-dipolar addition of the intermediate (**6**) to a second molecule of chloral⁸ (Scheme 2). This intermediate might also undergo an intramolecular cyclization to (**3a**).

In conclusion, this work reveals for the first time that easily available heterosubstituted methyleneketenes undergo intermolecular cycloaddition with chloral. This reaction provides a new access to α -methylene propiolactones whose synthesis has been reported only recently.⁹ We are currently investigating the reactivity of (**2**) with other heteronuclear double bonds.

[†] Selected data (IR in CHCl₃; ¹H NMR in CDCl₃ at 300 MHz unless noted otherwise, *J* in Hz): (*E*)-(**3a**): m.p. 76 °C; ν_{\max} . 1830 and 1710 cm⁻¹; δ_{H} 3.97 (s, 3H), 5.33 (d, 1H, *J* 1.3), and 7.15 (d, 1H, *J* 1.3). (*Z*)-(**3a**): m.p. 48 °C; ν_{\max} . 1830 and 1680 cm⁻¹; δ_{H} 4.12 (s, 3H), 5.24 (s, 1H), and 6.8 (s, 1H). (*E*)-(**3b**): m.p. 99 °C; ν_{\max} . 1800 and 1690 cm⁻¹; δ_{H} 2.36 (s, 3H), 3.84 (s, 3H), and 5.26 (s, 1H). (*Z*)-(**3b**): m.p. 68 °C; ν_{\max} . 1810 and 1660 cm⁻¹; δ_{H} 2.12 (s, 3H), 4.16 (s, 3H), and 5.22 (s, 1H). (**3c**): m.p. 162 °C; ν_{\max} . 1815 and 1620 cm⁻¹; δ_{H} 3.45–3.70 (m, 4H) and 5.25 (s, 1H). (*E*)-(**4a**): m.p. 172 °C; ν_{\max} . 1745 and 1640 cm⁻¹; δ_{H} (CD₃COCD₃) 4.15 (s, 3H), 5.52 (dd, 1H, *J* 0.75 and 0.3), 6.02 (d, 1H, *J* 0.3), and 7.51 (d, 1H, *J* 0.75). (*Z*)-(**4a**) (liquid): ν_{\max} . 1770 and 1640 cm⁻¹; δ_{H} (CD₃COCD₃) 4.15 (s, 3H), 5.0 (s, 1H), 6.15 (s, 1H), and 7.05 (s, 1H).

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