Tetrahedron Letters, Vol.31, No.9, pp 1261-1264, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

# REGIO- AND STEREOSELECTIVE RING-OPENING REACTIONS OF CYCLOPROPENONES: α-METHYLENE-γ-BUTYROLACTONES VIA ADDITIONS OF TRICHLOROCYCLOPROPENYLIUM IONS TO ALKENES

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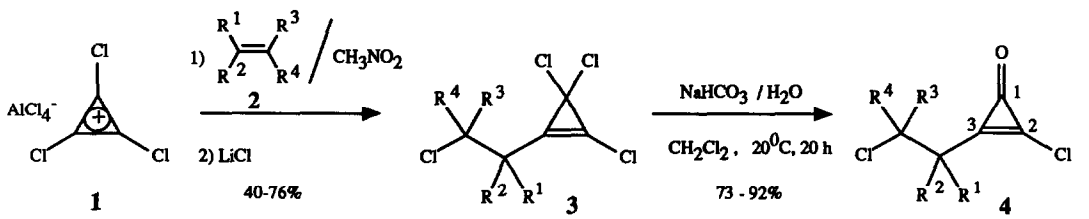
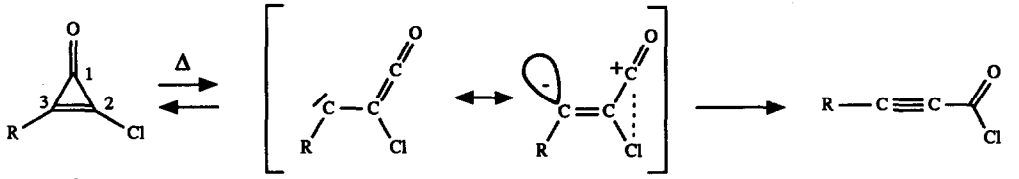
**Abstract.** *The 2-chloro-3-(2'-chloroalkyl)cyclopropenones **4**, readily obtained by hydrolysis of the adducts of the trichlorocyclopropenylium ion onto alkenes, thermally rearrange to propiolic acid chlorides **6**. Treatment of **4** with TosOH·$H_2O$ in $CH_2Cl_2$ yields the (E)-3-chloro-2-(2'-chloroalkyl)acrylic acids **9**, which have been converted in two simple steps to α-methylene-γ-butyrolactones **11** with good overall yields.*

Trichlorocyclopropenylium (**1**) salts usually react with alkenes **2** to give [1:2]- and [1:3]-products,[2] but in nitromethane solution, the selective formation of the [1:1]-adducts **3** has been accomplished.[3] The hydrolysis of 1-substituted trichlorocyclopropenes like **3** has been found to give the chlorocyclopropenones **4**.[3,4]




In this communication we report conditions to selectively cleave the C-1/C-3 bond or the C-1/C-2 bond of **4**, and we describe a novel access to α-methylene-γ-butyrolactones **11**.

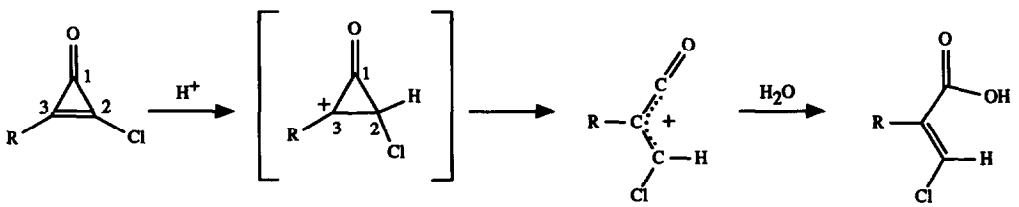
The 2-chloro-3-(2'-chloroalkyl)cyclopropenones **4** were obtained in 73-92% yield, when solutions of **3** in $CH_2Cl_2$ were stirred with aqueous $NaHCO_3$ solutions at ambient temperature. This procedure usually gives better yields than treatment of the neat trichlorocyclopropenes **3** with aqueous $NaHCO_3$.[3] Compounds **4** partially isomerize to the acid chlorides **6** when kept at room temperature for several days. An acceleration of this process by chloride ions ($R_4N^+Cl^-$) has not been found, but complete rearrangements of **4** to **6** were achieved (isolated yields: 75-90%) when neat samples of **4** were heated at $100^0C$ for 1 h. Though the carbenes **5** may be intermediates in this isomerisation,[4,5] we prefer a mechanism, in which migration of Cl begins, before the cleavage of the C-1/C-3 bond in **4** is complete.



**4** **5** **6**

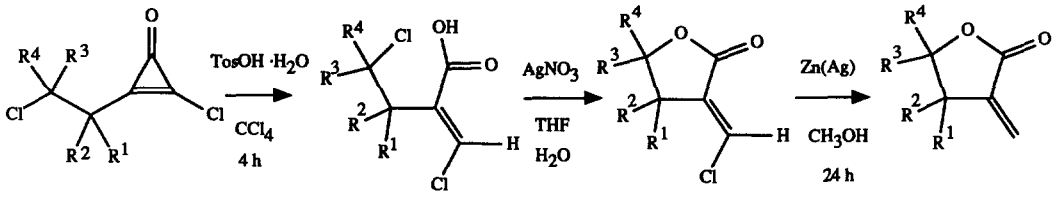
R = -CR¹R²-CR³R⁴Cl

Selective cleavage of the other single bond (C-1/C-2) in the cyclopropenone ring can be accomplished under acidic conditions, e. g. by stirring **4a-f** with $TosOH \cdot H_2O$ in $CCl_4$ at room temperature to produce single diastereoisomers of the acrylic acids **9a-f**. Their (*E*)-configuration has been derived from the coupling constant of 5.2 Hz between the vinylic hydrogen and the carbonyl carbon of **9e** ($^3J_{C,H}$). In analogy to this finding, 2-aryl-3-chlorocyclopropenones have been reported to yield (*E*)-2-aryl-3-chloroacrylic acids,[6a] and in one case the configuration of the resulting 3-chloroacrylic acid has been corroborated by X-ray structure analysis.[6b] Since alkyl groups are better electron donors than chlorine, initial protonation of **4** can be assumed to preferably take place at C-2, and the electrocyclic ring opening of the cyclopropyl cation **7** may then yield the allyl cation **8**, the precursor of **9**. The stereoselective formation of the (*E*)-configurated allyl cation **8** may be rationalized in a similar way as the ionisation of cyclopropyl derivatives under solvolytic conditions, in which the loss of the nucleofugal group is supported by the *exo*-disrotatory ring opening mode.[7] Analogously, one might assume that the rotation of the C-2/C-3 bond is initiated before protonation of **4** is complete, in which case **7** would not be an intermediate.[8]



**4** R = -CR¹R²-CR³R⁴Cl **7** **8** **9**

Treatment of the (*E*)-3-chloro-2-(2'-chloroalkyl)acrylic acids **9** with $AgNO_3$ in aqueous tetrahydrofuran[9] yields the α-(*E*)-chloromethylene-γ-butyrolactones **10** which can be dehalogenated with activated zinc powder in methanol[10] to give α-methylene-γ-butyrolactones **11** (see Table 1 and Scheme 1). Because of their interesting biological activities such compounds are presently under intensive investigation.[11-13]

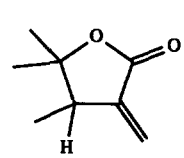



**4a-f** **9a-f** **10a-f** **11a-f**

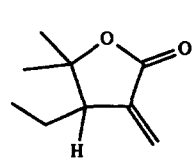
**Table 1.** Synthesis of the α-Methylene-γ-butyrolactones **11a-f** from **1** and the Alkenes **2a-f**.

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | **1+2a-f →** | **3a-f →** | **4a-f →** | **9a-f →** | **10a-f →** | **11a-f** |
|---|---|---|---|---|---|---|---|---|---|---|
| **a** | H | $CH_3$ | $CH_3$ | $CH_3$ | 61% | 73% | 73% | 61% | 81% | |
| **b** | H | $C_2H_5$ | $CH_3$ | $CH_3$ | 66% | 82% | 78% | 76% | 77% | |
| **c** | H | -$(CH_2)_4$- | | $CH_3$ | 54% | 92% | 48% | 63% | 78% | |
| **d** | H | $CH_3$ | -$(CH_2)_5$- | | 64% | 85% | 43% | 78% | 82% | |
| **e** | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | 76% | 82% | 92% | 68% | 80% | |
| **f** | $CH_3$ | -$(CH_2)_4$- | | $CH_3$ | 66% | 85% | 57% | 64% | 80% | |

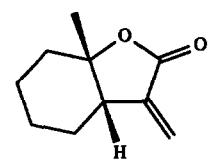
**Scheme 1.** Overall Yields of α-Methylene-γ-butyrolactones **11a-f** from **1** and Alkenes **2a-f**.



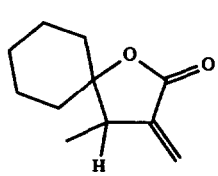
**11a**[11a] (16%)



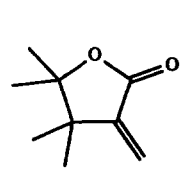
**11b** (25%)



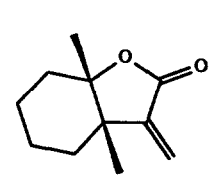
**11c**[11a] (12%)



**11d**[11a] (15%)

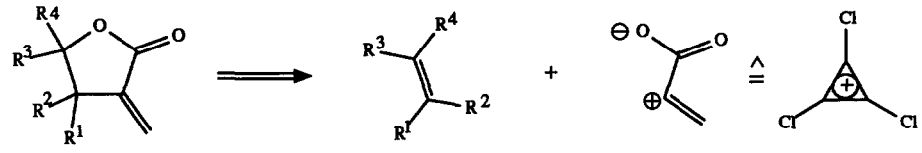


**11e**[11a,c] (32%)



**11f**[11d,14] (16%)

As α-methylenelactones **11a-f** (Scheme 1) are formed in 5 simple steps from **1** and the alkenes **2a-f** (12-32% overall yields), **1** may be considered to be a synthetic equivalent for the dipolar synthon **12**.



**11** **2** **12** **1**

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie as well as Hoechst AG.

**References and Notes.**

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**(Received in Germany 27 December 1989)**