Tetrahedron Letters, Vol.22, No.21, pp 1953 - 1956, 1981
Printed in Great Britain

0040-4039/81/211953-04$02.00/0

SYNTHESIS OF CYCLOBUTYLIDENEACETIC ESTERS VIA ALUMINUM CHLORIDE PROMOTED [2+2] CYCLOADDITIONS OF ETHYL 2,3-BUTADIENOATE TO OLEFINS+

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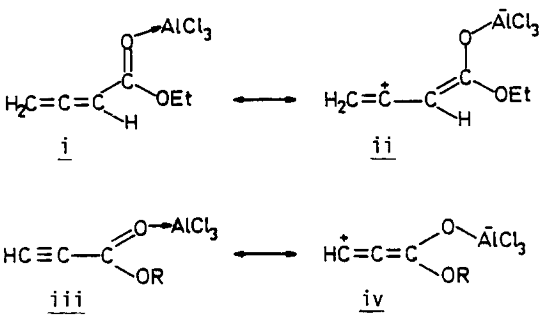
Summary: In the presence of $AlCl_3$*, ethyl 2,3-butadienoate reacts with a variety of olefins, including simple unactivated cycloalkenes, to give cyclobutylideneacetic esters at room temperature. The cycloaddition is regioselective and stereoselective.*

Cyclobutylideneacetic esters have hitherto attracted little attention, their formation having been mostly incidental in a study of the mechanism of some molecular rearrangements.[1] We report a simple route to these functionalized four-membered rings, using the $AlCl_3$-induced reaction of ethyl 2,3-butadienoate (1) with alkenes. Our work complements earlier studies of Lewis acid catalyzed cycloadditions of 2-propynoic esters to olefins.[2-4] As we had suggested[4] that the 2-propynoic ester-$AlCl_3$ complex behaves as a vinyl cation cum allenyl cation, formulated as iv, it was self-evident that a complexed allenic ester such as 1-$AlCl_3$ had to be tested as an electrophilic reagent. This ester can be formulated as i ⟷ ii (Scheme 1).



Scheme 1. Modified vinyl cations ii and iv by $AlCl_3$-complexation of allenic ester (1) and 2-propynoic ester, respectively.

In fact, the present letter was written when Snider reported his work on $EtAlCl_2$-catalyzed reactions of methyl 2,3-butadienoate with acyclic alkenes.[5]

The cycloadducts shown in Table 1 have been obtained by the following procedure. Ethyl 2,3-butadienoate (1) (1-2 g, 9-18 mmol) is dissolved in dried benzene (25 ml). Commercial aluminum trichloride (Merck) (0.5 molar equivalent with respect to 1) is vigorously stirred into the solution over a period of 15 min and the alkene (2 molar equivalent with respect to allenic ester 1) or cyclopentadiene is added. The progress of the reaction is monitored by pouring aliquots of the reaction solution into aqueous $NaHCO_3$/pentane, shaking the solution and examining the pentane phase by GC (SE 30 column). When the product peaks no longer increase

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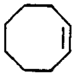
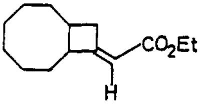
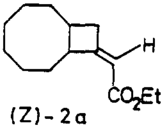
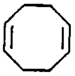
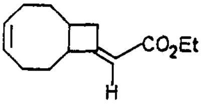
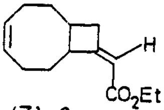
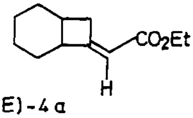
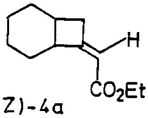
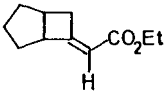
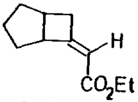
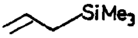
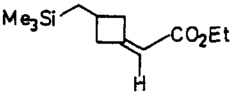
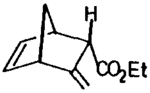
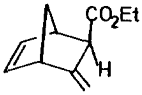
+ Dedicated to the memory of Franz Sondheimer.

Table 1. Cyclobutylideneacetic Esters via $AlCl_3$-Catalyzed Reaction of Ethyl 2,3-Butadienoate (1) with Alkenes.

Alkene	Cycloadducts		E : Z	Isolated Yield (%)[a]
 2	 (E)-2a	 (Z)-2a	91 : 9	29
 3	 (E)-3a	 (Z)-3a	93 : 7	50
 4	 (E)-4a	 (Z)-4a	90 : 10	14
 5	 (E)-5a	 (Z)-5a	92 : 8	35
 6	 6a		-	77
 7	 endo-7a	 exo-7a	86 : 14[b] (64 : 36)[d]	90-95[c]

[a] Yields (not optimized) after Kugelrohr distillation.

[b] endo : exo ratio.

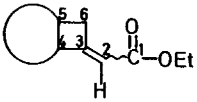
[c] In benzene the reaction takes 45 min at room temperature. In the absence of $AlCl_3$, refluxing is required.

[d] endo : exo ratio for cycloaddition in the absence of $AlCl_3$.

relative to 1, the reaction mixture is poured into aqueous $NaHCO_3$/pentane with precipitation of aluminum hydroxide, and the product is extracted continuously with a rotary perforator. The organic phase is washed with water until neutral and dried (Na_2SO_4). The solvent is evaporated to leave an oil which is distilled in a Kugelrohr apparatus.

Table 2. Spectroscopic and Other Data of Cycloadducts.

Numbering of Carbon Atoms:



(E)-2a: 90 MHz ^{1}H NMR ($CDCl_3$). δ 1.27 (t, J = 7 Hz, 3H), 1.3-1.8 (12H), 2.2-3.5 (m, 4H), 4.13 (q, J = 7 Hz, 2H), 5.6 (q, J = 2.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 170.3 (C=0), 166.6 (C-3), 111.6 (C-2), 59.4 (OCH_2), 48.0 d (C-4), 39.0 t (C-6), 36.7 d (C-5) 30.3, 29.9, 29.3, 26.4, 26.0, 25.8, 14.4 (CH_3). IR (neat) 1715, 1672 cm^{-1}. GC-MS (t_R 14.8min): m/e = 222 (M^+, 8%), 193(9), 177(26), 165(16), 149(26), 134(100), 126(12), 119(30), 111(21), 105(30), 91(50), 88(9), 79(50), 67(51), 55(30), 43(40). Calcd ($C_{14}H_{22}O_2$) C 75.63, H 9.99. Found C 75.66, H 9.79.

(Z)-2a: 90 MHz ^{1}H NMR ($CDCl_3$) δ inter al. 5.52 (q, resolved after addition of shift reagent). GC-MS (t_R 13.1min): m/e = 222 (M^+, 24%), 207(4), 193(26), 179(47), 165(34), 149(56), 134(90), 126(48), 119(48), 111(53), 107(54), 91(87), 79(97), 67(100), 55(70).

(E)-3a: 90 MHz ^{1}H NMR ($CDCl_3$). δ 1.26 (t, J = 7 Hz, 3H), 1.6-2.8 (10H), 2.9-3.3 (m, 2H, bridgehead H's), 4.15 (q, J = 7 Hz, 2H), 5.6 (m, 3H). ^{13}C NMR ($CDCl_3$). δ 170.1 (C=0), 166.3 (C-3), 130.4, 130.0, 111.5 d (C-2), 59.4 (OCH_2), 48.6 d (C-4), 37.7 t (C-6), 35.6 d (C-5), 30.7, 28.4, 26.0, 25.3, 14.5 (CH_3). IR (neat) 1715, 1670 cm^{-1}. GC-MS (t_R 7.6min): m/e = 220 (M^+, 4%), 205(2), 191(14), 174(17), 147(31), 137(17), 131(36), 119(40), 111(17), 105(69), 91 (100), 79(62), 67(38), 53(26). Calcd ($C_{14}H_{20}O_2$) C 76.33, H 9.15. Found C 76.44, H 9.18.

(Z)-3a: GC-MS (t_R 6.8min): m/e = 220 (M^+, 5%), 207(4), 191(12), 174(10), 151(12), 147(27), 131(33), 117(31), 105(66), 91(100), 79(69), 67(42), 53(36).

(E)-4a: 90 MHz ^{1}H NMR ($CDCl_3$). δ 1.28 (t, J = 7 Hz, 3H), 1.38-2.6 (m, 8H), 2.7-3.2 (m, 2H, bridgehead H's), 4.11 (q, J = 7 Hz, 2H), 5.6 (q, J = 2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 169.4 (C=0), 166.8 (C-3), 110.8 d (C-2), 59.6 (OCH_2), 42.7 d (C-4), 39.2 t (C-6), 29.6, 28.8, 24.3, 22.5, 21.7, 14.4 (CH_3). IR (neat) 1715, 1627 cm^{-1}. GC-MS (t_R 6.1min) m/e = 194 (M^+, 39%), 179(17), 165(48), 149(79), 133(54), 121(90), 105(68), 91(100), 79(93), 67(64), 53(35).

(Z)-4a: 90 MHz ^{1}H NMR ($CDCl_3$) δ inter al. 5.53 (q). GC-MS (t_R 5.8min) m/e = 194 (M^+, 19%), 179(11), 165(38), 151(60), 149(37), 137(36), 133(62), 105(64), 91(85), 79(100), 67(81), 55(52).

(E)-5a: 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.07-1.41 (t, J = 7 Hz, 3H), 1.52-1.96 (m, 6H), 2.30-2.52 (m, 4H), 3.96-4.30 (q, J = 7 Hz, 2H, OCH_2), 5.43-5.63 (q, J = 2 Hz, 1H). IR (neat) 1712, 1672 cm^{-1}. Calcd ($C_{11}H_{16}O_2$) C 73.3, H 8.95. Found C 73.42, H 9.05.

(Z)-5a: 90 MHz ^{1}H NMR ($CDCl_3$) δ inter al. 5.43 (m, resolved after addition of shift reagent).

(E+Z)-5a: MS (RT): m/e = 180 (M^+, 72%), 165(8), 152(100), 151(65), 137(25), 135(67), 134 (38), 133(24), 124(48), 123(42), 119(18), 111(19), 108(18), 107(92), 106(40), 105(42), 93(25), 92(26), 91(68), 79(98), 77(29), 67(41), 66(12), 65(19).

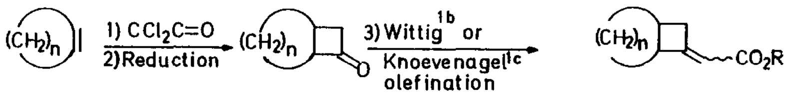
6a: 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.0 (s, 9H), 0.94 (d, J = 7 Hz, 2H), 1.26 (t, J = 7 Hz, 3H), 2.2-4.5 (m, 5H), 4.11 (q, J = 7 Hz, 2H), 5.57 (m, 1H). ^{13}C NMR ($CDCl_3$ δ 166.5 (C=0), 164.3 s (C-3), 112.3 d (C-2), 59.4 (OCH_2), 42.7 t (C-4), 41.6 t (C-6), 28.1 d (C-5), 25.4 t (C-7), 14.3 (CH_3), -1.27 ($SiMe_3$). IR ($CHCl_3$) 1703, 1670 cm^{-1}. Calcd ($C_{12}H_{22}O_2Si$) C 63.71, H 9.73. Found C 63.73, H 9.78.

endo-7 + exo-7: 90 MHz ^1H NMR ($CDCl_3$) δ 1.05-1.28 (2t, J = 7 Hz, $2CH_3$), 1.33-1.66 (m, $2CH_2$), 2.72 (q, 1H, endo-H), 3.1-3.3 (m, 4H, bridgehead H's), 3.3-3.44 (m, 1H, exo-H), 4.16-4.33 (2q, J = 7 Hz, 4H, $2OCH_2$), 4.86-5.03 (dd, 4H, $2CH_2=$), 6.11-6.27 (t, 4H, 2CH=CH).

Depending on the nucleophilicity of the alkene, the reaction takes less than 2h with 6 and up to several days with unactivated alkenes 2-5. The structure of the cyclobutylideneacetate products was corroborated by ^1H NMR, ^{13}C NMR and IR spectroscopy (Table 2). (E)- and (Z)-isomers were distinguished by GC-MS and by ^1H NMR, especially in the presence of shift reagent. In general, the (E)-isomers which have the ethoxycarbonyl grouping in a more accessible position than the (Z)-isomers, had the longer GC retention times and were also complexed more strongly with $Eu(fod)_3$.

The cyclobutylideneacetates 2a-5a are formed stereoselectively (E:Z ≥ 9:1), whilst cycloadduct 6a is formed regioselectively. Cyclopentadiene (7) and allenic ester 1 react to give the expected Diels Alder adduct 7a, also in the presence of $AlCl_3$. No four-membered adduct was detected. Thus, 1-$AlCl_3$ behaves as a conventional, but strongly activated dienophile towards 7, and only the nonterminal double bond reacts. 1-$AlCl_3$ is also more endo-selective than uncomplexed ethyl 2,3-butadienoate (1) (cf. Table 1).

Finally, the $AlCl_3$-promoted annelation of cycloalkenes with allenic esters serves as a convenient alternative to the three-step sequence: 1) Dichloroketene cycloaddition 2) Reductive removal of halogen and 3) Carbonyl olefination (Scheme 2). As allenic esters such as 1 are now readily accessible by the Wittig reaction [6], the one-pot annelation of cycloalkenes to cyclobutylideneacetates should be of preparative interest.



Scheme 2. Three-step annelation of cycloalkenes to cyclobutylideneacetic esters.

Acknowledgements. We thank Dr. F.J.Hammerschmidt of Dragoco for GC-MS measurements, Dr. E.Hofer for advice and assistance with NMR spectra and the Niedersächsische Minister für Wissenschaft und Kunst (Mittel aus dem Zahlenlotto) as well as the Fonds der Chemie for financial support.

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(Received in Germany 2 February 1981)