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Synthesis of 2-Arylidene Cycloalkane Carboxylates by Lead(IV) Acetate Perchloric Acid Assisted Ring Contraction of 2-Arylidene Cycloalkanones in Triethyl Orthoformate

Felix Mathew and Bekington Myrboh*

Department of Chemistry, North-Eastern Hill University, Shillong, Meghalaya, India-793 003, Tel.: +91 364 226593; Fax +91 364 760076

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Abstract

2-Arylidene cycloalkane carboxylates (**2**) are conveniently prepared from 2-arylidene cycloalkanones (**1**) using lead tetraacetate in the presence of perchloric acid in triethyl orthoformate.

Keywords: Arylidene cycloalkane carboxylates, ring contraction, 2-arylidene cycloalkanones.

Introduction

Methylene cycloalkanes are widely used as key intermediates in the synthesis of various natural substances and their analogs, e.g. prostaglandin [1a], irridoids [1b,c], antibiotics [2] and as models in investigations of addition reactions on the C=C bonds. The known methods for the preparation of methylene cyclanes may be divided into three major classes: (1) mainly pyrolytic elimination reactions [3a], (2) cyclisation and oligomerisation of some unsaturated compounds, e.g. allenes and α,ω-dienes [3a], (3) Wittig and related reactions [2a-b]. However, many of them including other methods found in the literature [4], have certain limitations. This prompted us to search for new and effective ways of synthesizing of this class of compounds.

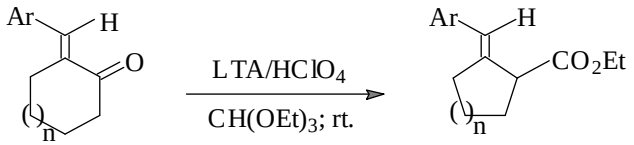
We have previously reported the use of the lead(IV) acetate-boron trifluoride etherate system in the conversion of acetophenones to methyl aryl acetates, in the ring contraction of tetralones to methyl indane-1-carboxylates and in the conversion of α,β-unsaturated ketones to β,γ-unsaturated carboxylates [5]. Cekovic and Cvetkovic also reported a closely related reaction using $Pb(OAc)_4$–$BF_3{\cdot}OEt_2$ [4g].

Here we wish to report the extension of the work leading to the synthesis of the titled compounds.

Results and Discussion

When the compound **1a** is subjected to lead(IV) acetate oxidation in the presence of boron trifluoride etherate and methanol in benzene, only trace amounts of the product **2a** can be isolated (Scheme 1). However, when $BF_3.OEt_2$ and methanol are replaced by perchloric acid and triethyl orthoformate, respectively, a smooth ring contraction takes place to give the product **2a** in moderate yields. It may be noted that triethyl orthoformate also serves as the solvent in all these reactions. The method is attractive since the reagents used are cheap and easily available.

* *To whom correspondence should be addressed*



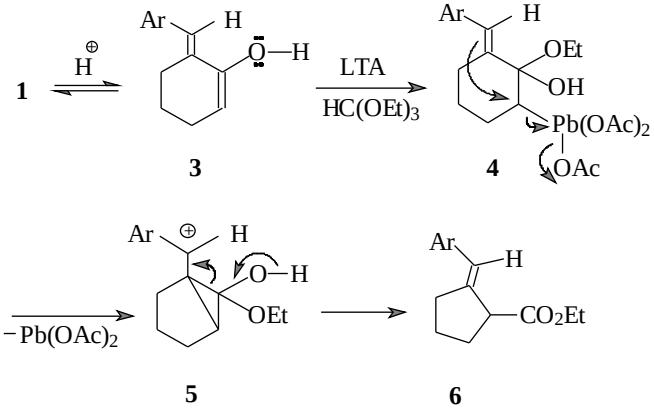
1 **n = 1, 2 and 3** **2**

Scheme 1

The probable mechanism is shown in Scheme 2. The individual steps involve the initial acid-catalyzed enolization of the ketone **1** followed by oxyplumbation of the C=C bond thus formed(cf oxythallation of alkyl aryl ketone) [6,4g]. Generation of the carbocation **5** with the anchimeric assistance of the neighbouring π-electrons, simultaneous reduction of lead(IV) to lead(II) and subsequent rearrangement lead to the product **6**. We are currently investigating the possibility of quenching the carbocation **5** with a view to isolating the bicyclic intermediate which has an intact cyclopropane ring.

Conclusions

2-arylidene cycloalkane carboxylates (**2**) are conveniently prepared from 2-arylidene cycloalkanones (**1**) using lead tetraacetate in the presence of perchloric acid in triethyl orthoformate. We will further investigate the remaining steriochemical problem in our work.



Scheme 2

Table 1

Entry	Product (**2**)*	Ar	n	Yields** (%)
1	a	C_6H_5	1	75
2	b	4-ClC_6H_4	1	72
3	c	2-ClC_6H_4	1	69
4	d	C_6H_5	2	67
5	e	4-ClC_6H_4	2	65
6	f	2-ClC_6H_4	2	61
7	g	C_6H_5	3	65
8	h	4-ClC_6H_4	3	60
9	i	2-ClC_6H_4	3	58
10	j	4-$CH_3C_6H_4$	1	77

** Products **2a-i** are all colorless viscous liquids*
*** Isolated yields*

Experimental Section

General remarks and materials

The 2-arylidene cycloalkanones **1a - i** were prepared according to the literature [7]. Lead tetraacetate was prepared and recrystallized and triethyl orthoformate was distilled before use. Chromatography was performed on silica gel 60. ^{1}H- and ^{13}C-NMR spectra were recorded at 300 MHz on a Bruker AC 300F spectrometer. Chemical shifts are given in ppm with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer 983 and are given in cm^{-1}. Microanalytical data were obtained on a Perkin-Elmer 2400 CNH elemental analyser.

General procedure

To a suspension of lead(IV) acetate (9g, 20 mmol) in triethyl orthoformate (30 ml), a solution of **1** (20 mmol) in 20 ml triethyl orthoformate and perchloric acid (3 ml) was added sequentially under stirring. The reaction mixture was stirred at room temperature for 24 h. The triethyl orthoformate was distilled off under reduced pressure and the residue treated with chloroform. The precipitate formed was filtetred off and the filtrate washed with water (2x100 ml), dried (Na_2SO_4) and evaporated. The crude product was purified by column chromatography using hexane as eluent to give **2** in high isolated yields (Table 1).

*Ethyl 2-(phenyl methylene)cyclopentane carboxylate (**2a**).*

Colorless viscous liquid, IR (neat), 1735, 1625 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 1.28(t, 3H, J=7.2 Hz, -CH_3), 1.69-2.08 (m,

4H, $-CH_2-CH_2-$), 2.63 (m, 2H, $-CH_2-$), 3.50 (m, 1H, -CH-), 4.18 (q, 2H, $-OCH_2-$), 6.52 (s,1H, vinylic), 7.30 (m, 5 ArH); ^{13}C-NMR, δ 14.28, 25.93, 29.44, 31.53, 51.13, 60.62, 123.66, 127.16, 128.18, 128.33, 138.03, 143.93, 174.36; Annal. Calculated, C, 78.22; H, 7.87; Found, C, 78.34; H, 7.93%.

*Ethyl 2-(4-chlorophenyl methylene)cyclopentane carboxylate (**2b**).*

Colorless viscous liquid, IR (neat), 1736, 1625 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 1.29 (t, 3 H, $-CH_3$), 1.69-2.08 (m, 4 H, $-CH_2-CH_2-$), 2.63 (m, 2 H, $-CH_2-$), 3.50 (m, 1 H, -CH-), 4.18 (q, 2 H, $-OCH_2-$), 6.52 (q, 1 H, vinylic), 7.30 (m, 4 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.26, 25.93, 29.48, 31.52, 51.21, 60.61, 123.60, 128.20, 130.31, 132.04, 136.03, 140.81, 173.75; Annal. Calculated, C, 68.04; H, 6.47; Found, C, 68.23; H, 6.59%.

*Ethyl 2-(2-chlorophenyl methylene)cyclopentane carboxylate (**2c**).*

Colorless viscous liquid, IR (neat), 1738, 1625 $cm^{-1;}$ ^{1}H-NMR ($CDCl_3$), δ 1.30 (t, J=7.2 Hz, 3 H, $-CH_3$), 2.01 (m, 4 H, $-CH_2-CH_2-$), 2.65 (m, 2 H, $-CH_2-$), 3.51 (m, 1 H, -CH-), 3.72 (q, 2 H, $-OCH_2-$), 6.54, 1 H, vinylic), 7.30 (m, 4 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.26, 25.95, 29.46, 31.53, 51.25, 60.65, 123.65, 127.14, 127.21, 127.85, 129.17, 135.93, 136.03, 140.81, 173.65; Annal. Calculated, C, 68.04; H, 6.47; Found, C, 68.21; H, 6.53%.

*Ethyl 2-(phenyl methylene) cyclohexane carboxylate (**2d**).*

Colorless viscous liquid, IR (neat), 1736, 1628 cm^{-1}; ^{1}H-NMR ($CDCL_3$), δ 1.29 (t, J=7.6 Hz, 3 H, $-CH_3$), 1.63 (m, 6 H, $-CH_2-CH_2-CH_2-$), 2.41 (m, 2 H,$-CH_2-$), 3.24 (m, 1 H, -CH-), 4.21 (q, 2 H, $-OCH_2-$), 6.21 (1 H, vinylic), 7.21 (m, 5 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.32, 23.60, 27.31, 27.86, 30.49, 50.98, 60.45, 123.62, 127.15, 128.18, 128.34, 138.03, 144.01, 174.36; Annal. Calculated, C, 78.65; H, 8.25; Found, C, 78.69; H, 8.31%.

*Ethyl 2-(4-chlorophenyl methylene)cyclohexane carboxylate (**2e**).*

Colorless viscous liquid, IR (neat), 1735, 1625 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 1.28 (t, J=7.2 Hz, 3 H, $-CH_3$), 1.61 (m, 6 H, $-CH_2-CH_2-CH_2-$), 2.40 (t, J=6.0 Hz, 2 H, $-CH_2-$), 3.23 (br t, 1 H, -CH-), 4.20 (q, 2 H, $-OCH_2-$), 6.20 (1 H, vinylic), 7.11-7.27 (m, 4 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.30, 23.59,27.29, 27.84, 30.46, 50.97, 60.47, 123.60, 128.20, 130.31, 132.04, 136.03, 140.61, 173.65; Annal. Calculated, C, 68.93; H, 6.86; Found, C, 68.75; H, 6.63%.

*Ethyl 2-(2-chlorophenyl methylene)cyclohexane carboxylate (**2f**).*

Colorless viscous liquid, IR(neat), 1736, 1624 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 1.28(t, 3 H, J=7.2 Hz, $-CH_3$), 1.59-2.13 (m, 6 H, $-CH_2-CH_2-CH_2-$), 2.63 (t, J=6.0 Hz, 2 H, $-CH_2-$), 3.50 (m, 1 H, -CH-), 4.18(q, 2 H, $-OCH_2-$), 6.52(q, 1H, vinylic), 7.11-7.27 (m, 4 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.30, 23.61, 27.31, 27.85, 30.45, 50.98, 60.49, 123.63, 127.15, 127.23, 127.91, 129.18, 135.93, 136.05, 140.83, 173.89; Annal. Calculated, C, 68.93; H, 6.86; Found, C, 68.69; H, 6.93%.

*Ethyl 2-(phenyl methylene) cycloheptane carboxylate (**2g**).*

Colorless viscous liquid, IR (neat), 1736, 1625 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 1.25 (t, J=7.2 Hz, 3 H, $-CH_3$), 1.42 (m, $-CH_2-CH_2-$), 1.84 (m, 8 H, $-CH_2-CH_2-CH_2-CH_2-$), 2.41 (m, 2 H, $-CH_2-$), 3.34 (m, 1 H, -CH-), 4.15 (q, 2 H, $-OCH_2-$), 6.39 (1 H, vinylic), 7.26-7.29 (m, 5 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.23, 26.48, 28.67, 29.20, 29.94, 30.43, 53.59, 60.42, 126.36, 128.15, 128.59, 128.86, 137.72, 141.95, 174.74; Annal. Calculated, C, 79.02; H, 8.58; Found, C, 78.98; H, 8.64%.

*Ethyl 2-(4-chlorophenyl methylene)cycloheptane carboxylate (**2h**).*

Colorless viscous liquid, IR (neat), 1734, 1628 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 1.26 (t, J=7.2Hz, 3 H,$-CH_3$), 1.40 (m, 4 H, $-CH_2-CH_2-$), 1.85 (m, 8 H, $-CH_2-CH_2-CH_2-CH_2-$), 2.42 (m, 2 H, $-CH_2-$), 3.34 (br t, 1 H, -CH-), 4.16 (q, 2 H, $-OCH_2-$), 6.40 (1 H, vinylic), 7.28-7.31 (m, 4 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.23, 26.50, 28.70, 29.22, 29.96, 30.48, 53.62, 60.49, 126.60, 128.20, 130.31, 132.05, 136.08, 140.20, 174.56; Annal. Calculated, C, 69.73; H, 7.23; Found, C, 69.63; H, 7.32%.

*Ethyl 2-(2-chlorophenyl methylene)cycloheptane carboxylate (**2i**).*

Colorless viscous liquid, IR (neat), 1736, 1625 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 1.28 (t, J=7.0 Hz, 3 H, $-CH_3$), 1.40 (m, 4 H, $-CH_2-CH_2-$), 1.89 (m, 8 H, $-CH_2-CH_2-CH_2-CH_2-$), 2.46 (m, 2 H, $-CH_2-$), 3.38 (m, 1 H, -CH-), 4.16 (q, 2 H, $-OCH_2-$), 6.42 (1 H, vinylic), 7.30-7.32 (m, 4 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.26, 26.49, 28.62, 29.26, 29.96, 30.44, 53.68, 60.48, 125.32, 127.18, 127.23, 127.98, 129.15, 136.00, 136.08, 140.88, 174.81; Annal. Calculated, C, 69.73; H, 7.23; Found, C, 69.53; H, 7.11%.

*Ethyl 2-(p-tolyl methylene)cyclopentane carboxylate (**2j**).*

Colorless viscous liquid, IR (neat) 1732, 1624 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 1.28 (t, J=7.2 Hz, 3 H, $-CH_3$), 1.69-2.08

(m, 4 H, -CH_2-CH_2-), 2.32 (s, 3 H, -CH_3), 2.62 (m, 2 H, -CH_2-), 3.51 (m, 1 H, -CH-), 4.20 (q, 2 H, -OCH_3), 6.52 (1 H, vinylic), 7.32 (m, 5 ArH); ^{13}C-NMR ($CDCl_3$), δ 14.30, 21.32, 26.01, 29.50, 31.52, 51.25, 60.65, 123.62, 129.10, 130.52, 132.04, 137.80, 141.21, 173.68; Annal. Calculated, C, 78.63; H, 8.26; Found, C, 78.41; H, 8.48%.

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