

Organometallic Chemistry

Synthesis and transformations of metallacycles

20.* Cp₂ZrCl₂-Catalyzed cycloalumination of arylolefins with AlEt₃

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The Cp₂ZrCl₂-catalyzed reaction of arylolefins (styrene, *o*- and *p*-methylstyrenes, *trans*-stilbene, 1,4-diphenyl-1,3-butadiene) with AlEt₃ resulting in mono- and disubstituted alumacyclopentanes and substituted alumacyclopropanes was studied. The yield and ratio of cyclic organoaluminum compounds depend on the structure of the initial arylolefins and conditions of cycloalumination.

Key words: organoaluminum compounds, alumacyclopentanes, zirconium complexes, arylolefins.

Catalytic cycloalumination of aliphatic α -olefins with trialkyl- or alkylhaloalanes in the presence of Zr complexes affords 3- and *trans*-3,4-substituted alumacyclopentanes in virtually quantitative yields.^{2,3}

In a continuation of studies of the reaction of olefin cycloalumination discovered by us² and to extend this method to other unsaturated compounds, in particular, arylolefins, and reveal the effect of aryl substituents on the direction of the reaction, we investigated cyclometalation of styrene, *o*- and *p*-methylstyrenes, *trans*-stilbene, and 1,4-diphenyl-1,3-butadiene with AlEt₃ using Cp₂ZrCl₂ as the catalyst.

Results and Discussion

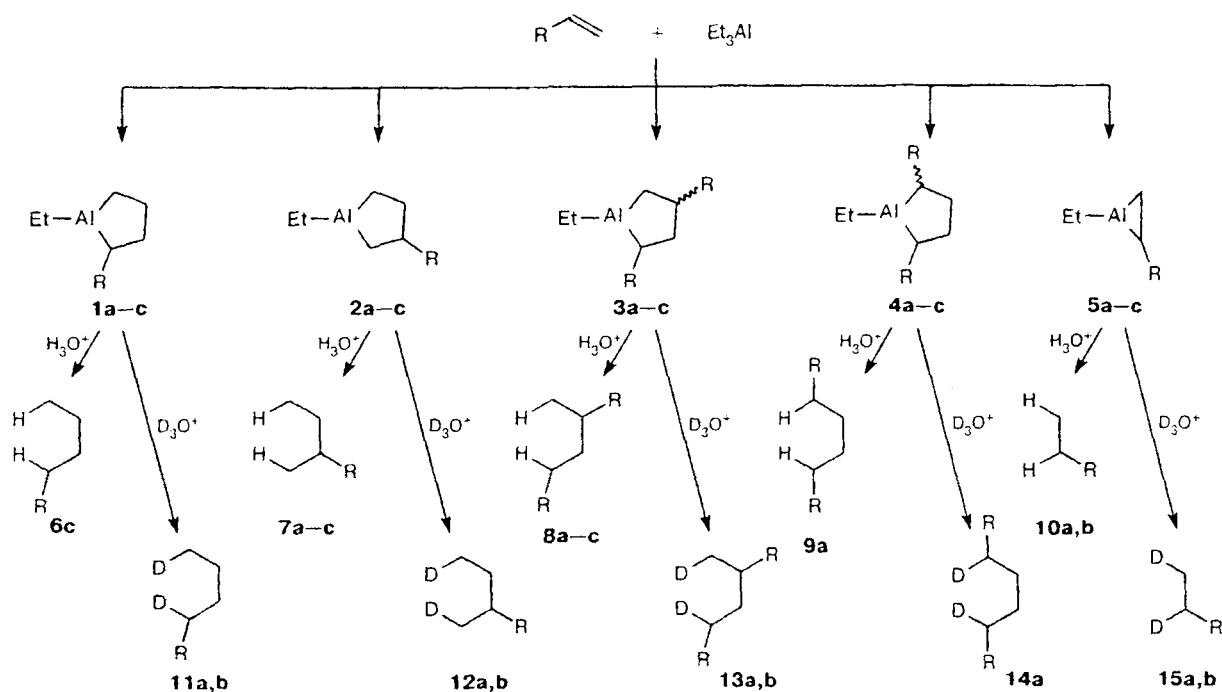
The reaction of styrene with AlEt₃ (1 : 1.2) in the presence of 5 mol.% Cp₂ZrCl₂ affords 1-ethyl-2-phenyl-

(**1a**), 1-ethyl-3-phenyl- (**2a**), 1-ethyl-2,4-diphenyl- (**3a**), 1-ethyl-2,5-diphenylalumacyclopentanes (**4a**) and 1-ethyl-2-phenylalumacyclopropane (**5a**) in a ratio of ~50 : 25 : 15 : 3 : 7 in an overall yield >90% (according to GLC data of the hydrolysis products of compounds **1a**–**5a**) (Scheme 1). The structure of hydrolysis products (**6**–**15**) was established from the data of ¹³C and ¹H NMR spectroscopy. Thus, cycloalumination of styrene proceeds less selectively than that of aliphatic α -olefins and results in a mixture of cyclic organoaluminum compounds (OAC).

Probably, intermediate Zr π -complexes (**16a,b**)^{4,5} are formed under the reaction conditions (Scheme 2), and they are responsible for the formation of the corresponding regioisomeric alumacyclopentanes. Attempts to determine the configuration of phenyl substituents in five-membered OAC were unsuccessful because of broadening of the signals of C(2) and C(5) atoms in the ¹³C NMR spectra of compounds **3a** and **4a**.

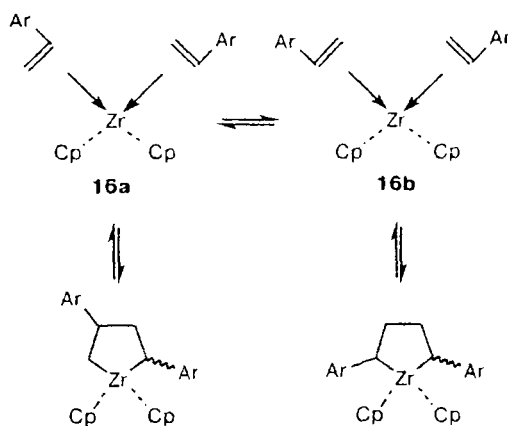
* For Part 19, see Ref. 1.

Scheme 1



a: R = Ph; b: R = *p*-MePh; c: R = *o*-MePh

Scheme 2



Based on the results obtained, we assumed that zirconacyclopentane intermediates (**17**)^{6–8} are initially formed, which are then transmetalated into alumacyclopentanes **5**. The insertion of the initial styrene molecule at the active Zr–C bond of the zirconacyclopentane intermediates results in mono- or disubstituted zirconacyclopentanes, and their transmetalation affords cyclic OAC **1–4** (Scheme 3).

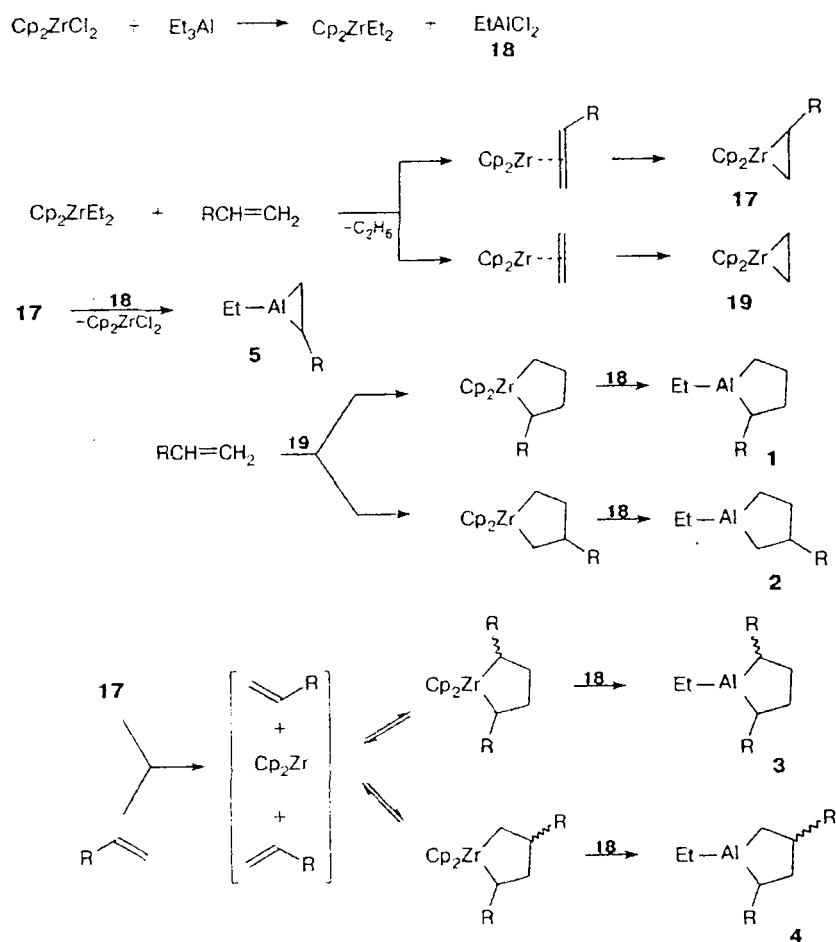
It cannot be ruled out that cyclic OAC **1–5** are formed along with the formation of intermediate Zr- and Al-containing bimetallic complexes^{9–12} generated under the reaction conditions from zirconacycloalkanes and aluminum halides (Scheme 4). In favor of this assumption are the syntheses of substituted alumacyclopentanes^{3,13} and alumacyclopentanes¹⁴ from RAICl₂ and α -olefins in the presence of halide ion acceptors (Mg, Ca, and Na) and catalytic amounts of Cp₂ZrCl₂, ZrCl₄, or Cp₂TiCl₂.

Cycloaluminum of *o*- and *p*-methylstyrenes also results in a mixture of substituted cyclic OAC **1–5** in 75–85% yields and with approximately the same ratios as for styrene.

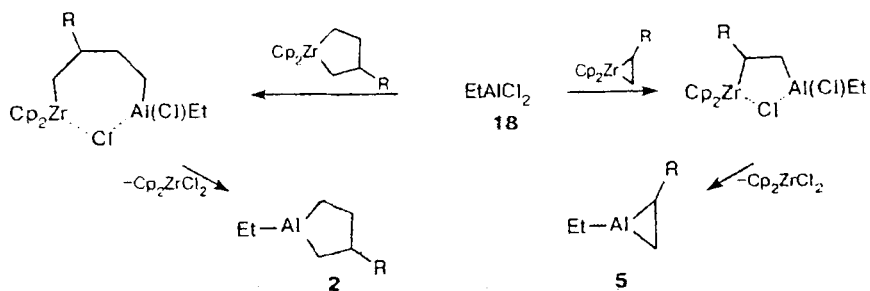
trans-Stilbene is virtually inactive in the reaction with AlEt₃. Under the conditions found, 1,4-diphenyl-1,3-butadiene reacts with AlEt₃ in the presence of Cp₂ZrCl₂ to give trisubstituted alumacyclopentane (**20**) in ~15% yield (Scheme 5). However, when Cp₂ZrCl₂ is replaced by Cp₂TiCl₂, AlEt₃ is replaced by EtAlCl₂, and Mg is introduced as the acceptor of Cl[–], compound **20** is formed¹⁴ from 1,4-diphenylbuta-1,3-diene in ~80% yield.

The results obtained suggest that, unlike aliphatic α -olefins, which react with AlEt₃ in a Cp₂ZrCl₂-catalyzed reaction to form 3-alkylalumacyclopentanes² with high regioselectivity, 1-arylolefins give under these conditions a mixture of substituted three- and five-membered OAC.

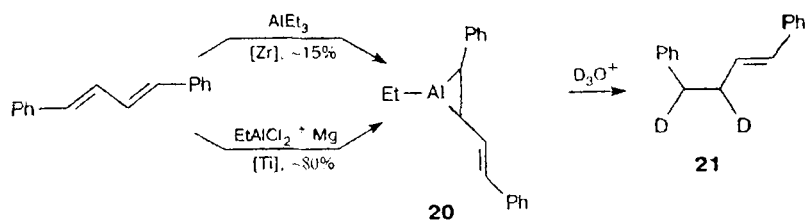
Scheme 3



Scheme 4



Scheme 5



Experimental

Cycloaluminum of arylolefins was carried out in an atmosphere of dry argon. Hydrolysis products were analyzed on a Chrom-41 chromatograph with He as the carrier gas using a 1200×3 mm column with 5% SE-30 or 15% PEG-6000 on Chromaton N-AW and a katharometer as the detector. IR spectra were recorded on a UR-20 spectrometer (thin film), and EI mass spectra were obtained on an MKh-1306 spectrometer (70 eV) at 130 °C. ¹H NMR spectra were recorded in CDCl₃ on a Tesla BS-567 spectrometer (100 MHz) using Me₄Si as the internal standard, and ¹³C NMR spectra were obtained in CDCl₃ on a Jeol FX-90Q spectrometer (22.5 MHz) with broad-band and off-resonance proton decoupling. ¹³C NMR spectra of cyclic OAC were obtained on Jeol FX-90Q (22.5 MHz) and Bruker AM-300 (75.46 MHz) spectrometers in regimes with full and partial proton decoupling. Dilute solutions in diethyl ether were used with addition of C₆D₆ for internal field stabilization. Solutions were placed in sealed tubes and then in an atmosphere of dry argon. Me₄Si was used as the internal standard. Yields of cyclic OAC were determined by GLC analysis of hydrolysis products.

Cycloaluminum of arylolefins with AlEt₃ in the presence of Cp₂ZrCl₂ (general procedure). Cp₂ZrCl₂ (0.5 mmol), arylolefin (10 mmol), and AlEt₃ (12 mmol) were placed in a glass reactor in an atmosphere of dry argon at 0 °C. The solution was warmed to 22–23 °C and stirred for 12 h. The reaction mixture was treated with 5% HCl or 20% DCl in D₂O, and the products were extracted with ether and isolated by distillation. The nomenclature of atoms of the cyclic OAC obtained and their hydrolysis products is presented in Fig. 1. The ¹³C NMR spectra and physicochemical constants are presented in Table 1.

Butylbenzene (6a), b.p. 58–59 °C (6 Torr), *n*²²_D 1.4893. IR, *v*/cm⁻¹: 695, 730, 1450, 1490, 1600, 2910, 2945, 3010, 3045. ¹H NMR, δ: 0.95 (t, 3 H, CH₃, *J* = 7.5 Hz); 1.23–1.75 (m, 4 H, CH₂); 2.60 (t, 2 H, CH₂Ph, *J* = 7.5 Hz); 6.8–7.32 (m, 5 H, CH arom.). MS, *m/z*: 134 [M]⁺. Found (%): C, 89.47; H, 10.40. C₁₀H₁₄. Calculated (%): C, 89.55; H, 10.45.

***p*-Butyltoluene (6b)**, b.p. 65 °C (4 Torr), *n*²²_D 1.4908. IR, *v*/cm⁻¹: 690, 710, 765, 1375, 1465, 1500, 1610, 1800, 1870, 1940, 3030, 3070. ¹H NMR, δ: 0.86 (t, 3 H, Me, *J* = 7.4 Hz); 1.20–1.80 (m, 4 H, CH₂); 2.26 (s, 3 H, CH₃Ph); 2.55 (t, 2 H, CH₂Ph, *J* = 7.1 Hz); 6.8–7.32 (m, 4 H, CH arom.). MS, *m/z*: 148 [M]⁺. Found (%): C, 89.11; H, 10.76. C₁₁H₁₆. Calculated (%): C, 89.19; H, 10.81.

***o*-Butyltoluene (6c)**, b.p. 62–63 °C (4 Torr), *n*²²_D 1.4950. IR, *v*/cm⁻¹: 720, 900, 1010, 1450, 2850, 2940, 3000, 3350. ¹H NMR, δ: 0.87 (t, 3 H, Me, *J* = 7.4 Hz); 1.18–1.76 (m, 4 H, CH₂); 2.23 (s, 3 H, CH₃-Ph); 2.28–2.40 (m, 2 H, CH₂Ph); 7.02–7.30 (m, 4 H, CH₂ arom.). MS, *m/z*: 148 [M]⁺. Found (%): C, 89.21; H, 10.73. C₁₁H₁₆. Calculated (%): C, 89.19; H, 10.81.

***sec*-Butylbenzene (7a)**, b.p. 49–50 °C (6 Torr), *n*²²_D 1.4894. IR, *v*/cm⁻¹: 695, 730, 1450, 1490, 1600, 2910, 2945, 3010, 3045. ¹H NMR, δ: 0.85 (m, 3 H, Me); 1.43–1.65 (m, 2 H, CH₂); 1.27 (d, 3 H, Me, *J* = 7.3 Hz); 2.52–2.71 (m, H, CH); 7.21 (m, 5 H, CH arom.). MS, *m/z*: 134 [M]⁺. Found (%): C, 89.59; H, 10.39. C₁₀H₁₄. Calculated (%): C, 89.55; H, 10.45.

***p*-*sec*-Butyltoluene (7b)**, b.p. 58–59 °C (4 Torr), *n*²²_D 1.4930. IR, *v*/cm⁻¹: 700, 1470, 1530, 1600, 1820, 1872, 1945, 3032, 3068. ¹H NMR, δ: 0.95 (t, 3 H, Me, *J* = 7.1 Hz); 1.21 (d, 3 H, Me, *J* = 7.1 Hz); 1.43–1.65 (m, 2 H, CH₂); 2.25 (s, 3 H, CH₃Ph); 6.81–7.32 (m, 4 H, CH arom.). MS, *m/z*: 148 [M]⁺. Found (%): C, 89.13; H, 10.87. C₁₁H₁₆. Calculated (%): C, 89.19; H, 10.81.

***o*-*sec*-Butyltoluene (7c)**, b.p. 54–55 °C (4 Torr). IR, *v*/cm⁻¹: 720, 900, 1010, 1360, 1450, 1490, 1600, 2850, 2940, 3000. ¹H NMR, δ: 0.87–0.95 (m, 3 H, Me); 1.22 (d, 3 H, Me, *J* = 7.1 Hz); 1.48–1.65 (m, 2 H, CH₂); 2.23 (s, 3 H, CH₃Ph); 2.33–2.43 (m, 1 H, CHPh); 7.02–7.32 (m, 4 H, CH arom.). MS, *m/z*: 148 [M]⁺. Found (%): C, 89.22; H, 10.76. C₁₀H₁₄. Calculated (%): C, 89.19; H, 10.81.

1,3-Diphenylbutane (8a), b.p. 125–126 °C (2 Torr), *n*²²_D 1.5516. IR, *v*/cm⁻¹: 720, 800, 850, 1220, 1250, 1370, 1510, 1620, 3050, 3080. ¹H NMR, δ: 1.18 (d, 3 H, Me, *J* = 7.0 Hz); 1.77–1.88 (m, 2 H, CH₂); 2.35–2.67 (m, 3 H, CH-CH₂); 7.02–7.43 (m, 10 H, CH arom.). MS, *m/z*: 210 [M]⁺. Found (%): C, 91.35; H, 8.54. C₁₆H₁₈. Calculated (%): C, 91.43; H, 8.57.

1,3-Di(*p*-tolyl)butane (8b), b.p. 162 °C (2 Torr). IR, *v*/cm⁻¹: 700, 980, 1450, 1500, 1600, 1890, 2160, 2905, 2940. ¹H NMR, δ: 1.19 (d, 3 H, Me, *J* = 7.2 Hz); 1.76–1.90 (m, 2 H, CH₂); 2.24 (s, 6 H, CH₃Ph); 2.34–2.68 (m, 3 H, CH-CH₂); 6.83–7.41 (m, 8 H, CH arom.). MS, *m/z*: 238 [M]⁺. Found (%): C, 90.62; H, 9.19. C₁₈H₂₂. Calculated (%): C, 90.76; H, 9.24.

1,3-Di(*o*-tolyl)butane (8c), b.p. 169–170 °C (2 Torr). IR, *v*/cm⁻¹: 720, 800, 1500, 1600, 2850, 2940, 3000. ¹H NMR, δ: 1.21 (d, 3 H, Me, *J* = 6.8 Hz); 1.76–1.93 (m, 2 H, CH₂); 2.23 (s, 6 H, CH₃Ph); 2.33–2.66 (m, 3 H, CH-CH₂); 6.96–7.34 (m, 8 H, CH arom.). Found (%): C, 90.71; H, 9.20. C₁₈H₂₂. Calculated (%): C, 90.76; H, 9.24.

1,4-Diphenylbutane (9a), b.p. 144–145 °C (2 Torr). IR, *v*/cm⁻¹: 720, 1620, 3050, 3080. ¹H NMR, δ: 1.68–1.96 (m, 4 H, CH₂); 2.35–2.54 (m, 4 H, CH₂Ph); 6.83–7.41 (m, 10 H, CH arom.). Found (%): C, 91.32; H, 8.51. C₁₆H₁₈. Calculated (%): C, 91.43; H, 8.57.

Ethylbenzene (10a), b.p. 136–137 °C, *n*²²_D 1.4951. IR, *v*/cm⁻¹: 690, 730, 1020, 1450, 1490, 1595, 2850, 2950, 3010, 3020. ¹H NMR, δ: 1.19 (t, 3 H, Me, *J* = 7.6 Hz); 2.50 (q, 2 H, CH₂, *J* = 7.6 Hz); 7.05–7.20 (m, 5 H, CH arom.). MS, *m/z*: 106 [M]⁺. Found (%): C, 90.48; H, 9.39. C₈H₁₀. Calculated (%): C, 90.57; H, 9.43.

***p*-Ethyltoluene (10b)**, b.p. 62–63 °C (20 Torr), *n*²²_D 1.4942. IR, *v*/cm⁻¹: 710, 800, 1010, 1050, 1350, 1450, 1500, 1600, 2420, 2860, 2940, 3300. ¹H NMR, δ: 1.18 (t, 3 H, Me, *J* = 7.6 Hz); 2.24 (s, 3 H, CH₃Ph); 2.48 (q, 2 H, CH₂, *J* = 7.6 Hz). MS, *m/z*: 120 [M]⁺. Found (%): C, 89.91; H, 9.96. C₉H₁₂. Calculated (%): C, 90.00; H, 10.00.

(1,4-Dideuterobutyl)benzene (11a), b.p. 50–51 °C (4 Torr), *n*²⁰_D 1.4879. IR, *v*/cm⁻¹: 690, 750, 1430, 1500, 1600, 2160 (vCD), 2920, 2950, 3010, 3045. ¹H NMR, δ: 0.90 (t, 2 H, CH₃D, *J* = 7.1 Hz); 1.25–1.75 (m, 4 H, CH₂); 2.60 (t, H, CHD, *J* = 7.2 Hz); 7.00–7.46 (m, 5 H, CH arom.). MS, *m/z*: 136 [M]⁺. Found (%): C, 88.17; H, 11.68. C₁₀H₁₂D₂. Calculated (%): C, 88.24; H, 8.82; D, 2.94.

***p*-(1,4-Dideuterobutyl)toluene (11b)**, b.p. 70–71 °C (5 Torr), *n*²¹_D 1.4912. IR, *v*/cm⁻¹: 700, 760, 1375, 1465, 1500, 1800, 1870, 1940, 2170 (vCD), 3030, 3070. ¹H NMR, δ: 0.85 (t, 2 H, CH₃D, *J* = 7.4 Hz); 1.22–1.70 (m, 4 H, CH₂); 2.55 (t, 1 H, CHD, *J* = 7.2 Hz); 7.02–7.05 (m, 4 H, CH arom.). MS, *m/z*: 150 [M]⁺. Found (%): C, 79.92; H, 11.95. C₁₁H₁₄D₂. Calculated (%): C, 88.00; H, 9.33; D, 2.67.

(1,4-Dideutero-*sec*-butyl)benzene (12a), b.p. 53–54 °C (8 Torr), *n*²²_D 1.4895. IR, *v*/cm⁻¹: 680, 730, 1450, 1500, 1600, 2910, 2160 (vCD), 2950, 3020, 3050. ¹H NMR, δ: 0.80–1.03 (t, 2 H, CH₃D, *J* = 7.3 Hz); 1.27 (d, 2 H, CH₂D, *J* = 7.3 Hz); 1.46–1.75 (m, 2 H, CH₂); 2.52–2.71 (m, 1 H, CHPh); 6.80–7.30 (m, 5 H, CH arom.). MS, *m/z*: 136 [M]⁺. Found (%): C, 88.12; H, 11.71. C₁₀H₁₂D₂. Calculated (%): C, 88.24; H, 8.82; D, 2.94.

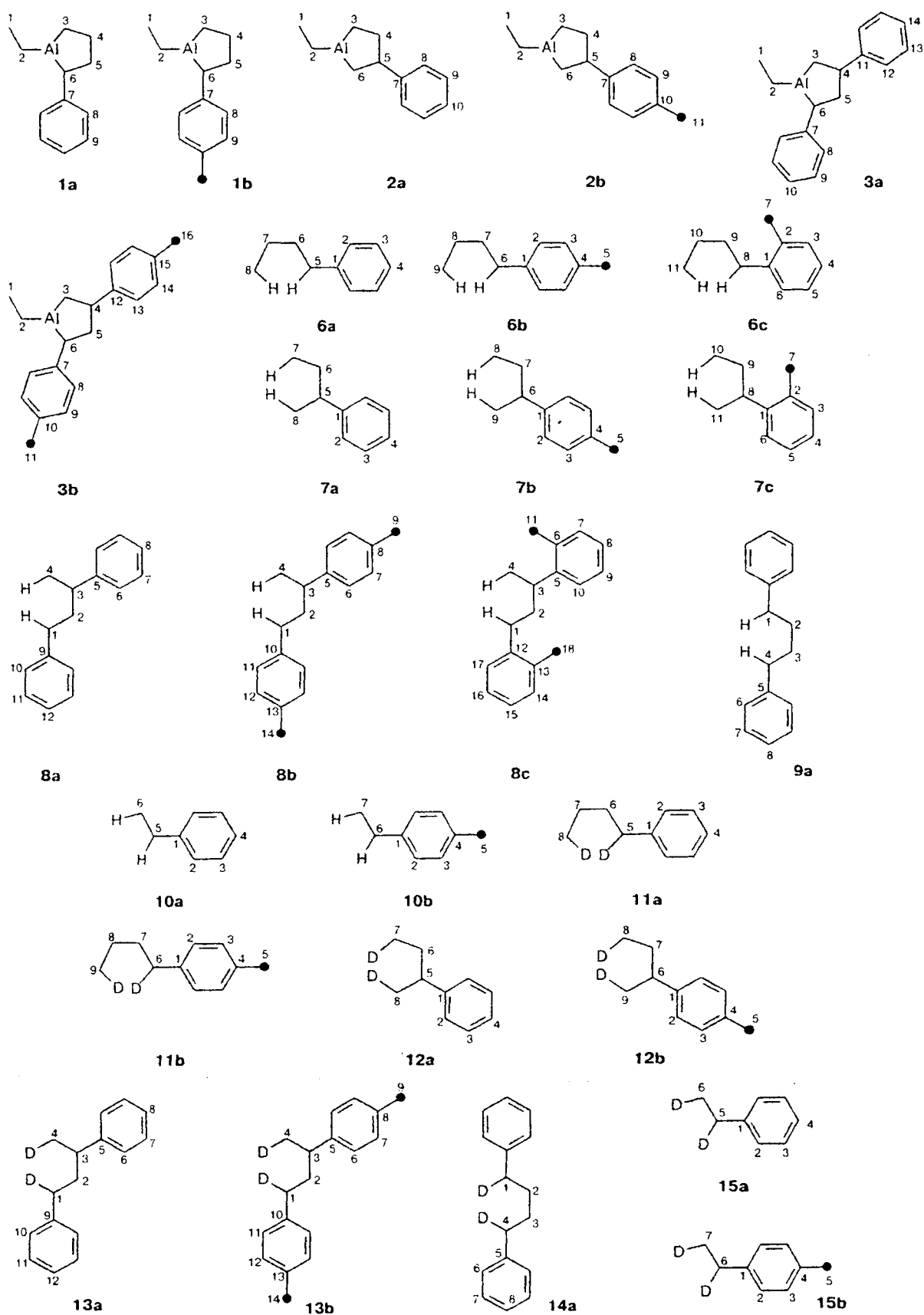


Fig. 1. Numeration of atoms in cyclic OAC and their hydrolysis products.

Table 1. ¹³C NMR spectra of cyclic OAC and hydrolysis products

Com- pound	δ ($J_{C,D}$ /Hz)															
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16
1a	9.06 q	0.48 br.t	10.28 br.t	31.50 t	32.99 t	25.57 br.d	147.96 s	128.65 d	126.63 d	125.53 d						
1b	9.06 q	0.68 br.t	10.55 br.t	28.83 t	32.08 t	27.47 br.d	144.71 s	129.17 d	129.17 d	137.30 s	21.09 q					
2a	9.06 q	0.48 br.t	8.54 br.t	35.59 t	46.13 d	17.84 br.t	149.72 s	128.65 d	128.65 d	125.92 d						
2b	9.06 q	0.68 br.t	7.95 br.t	35.72 t	45.80 d	17.90 br.t	146.66 s	126.50 d	129.17 d	137.30 s	21.09 q					
3a	8.93 q	0.74 br.t	13.48 br.t	44.05 d	42.75 t	27.98 br.d	140.69 s	128.52 d	128.52 d	126.37 d	143.28 s	127.61 d	127.61 d	126.37 d		
3b	9.12 q	1.00 br.t	13.74 br.t	48.47 d	42.29 t	28.70 br.d	140.29 s	128.52 d	128.52 d	137.10 s	20.96 q	147.10 s	126.37 d	128.52 d	137.69 s	20.96 q
6a	142.65 s	128.34 d	128.21 d	125.55 d	35.81 t	33.66 t	22.34 t	13.96 q								
6b	144.73 s	130.95 d	128.34 d	134.98 s	21.04 q	34.96 t	33.79 t	22.34 t	14.06 q							
6c	141.09 s	135.43 s	128.86 d	125.48 d	127.08 d	128.86 d	19.29 q	32.62 t	33.14 t	22.86 t	14.09 q					
7a	147.46 s	126.98 d	128.34 d	125.72 d	41.72 d	31.19 t	12.20 q	21.89 q								
7b	149.93 s	126.98 d	128.99 d	134.98 s	21.04 q	41.27 d	31.19 t	12.36 q	21.04 q							
7c	145.84 s	134.98 s	130.16 d	125.29 d	126.78 d	126.13 d	19.74 q	36.26 d	30.64 t	12.33 q	21.24 q					
8a	33.99 t	39.97 t	39.44 d	22.54 q	147.44 s	128.40 d	128.40 d	126.00 d	142.52 s	128.41 d	127.11 d	125.68 d				
8b	33.53 t	40.16 t	38.99 d	22.54 q	140.21 s	128.21 d	128.93 d	135.04 s	20.91 q	139.40 s	130.81 d	127.82 d	134.72 s	20.91 q		
8c*	31.32 t	40.29 t	34.31 d	22.73 q	145.19 s	135.24 s	130.03 d	125.16 d	126.20 d	126.91 d	21.69 q	140.57 s	135.63 s	128.67 d	126.20 d	125.16 d
9a	35.71 t	31.00 t	31.00 t	35.71 t	142.42 s	128.14 d	127.04 d	125.63 d								
10a	144.33 s	127.90 d	128.37 d	127.90 d	28.93 t	15.65 q										
10b	141.22 s	124.89 d	129.06 d	135.04 s	21.04 q	28.46 t	15.78 q									
11a	142.65 s	128.34 d	128.21 d	125.55 d	35.42 (19.1)	33.66 t	22.34 t	13.63 (19.1)								
11b	144.73 s	130.95 d	128.34 d	134.98 s	21.04 q	34.96 d	35.79 t	22.34 t	13.76 t							
12a	147.46 s	126.98 d	128.34 d	126.72 d	41.72 d	31.19 t	11.94 t	21.56 t								
12b	149.93 s	126.98 d	128.99 d	134.98 s	21.04 q	41.27 d	31.19 t	12.07 t	20.85 t							
13a	33.66 d	39.97 t	39.44 d	22.21 t	147.44 s	128.41 d	128.41 d	126.00 d	142.52 s	128.41 d	127.11 d	125.68 d				
13b	33.20 d	40.16 t	38.99 d	22.28 t	144.21 s	128.21 d	128.93 d	135.04 s	20.91 q	139.40 s	130.81 d	127.82 d	134.72 s	20.91 q		
14a	35.43 d	31.00 t	31.00 t	35.43 d	142.42 s	128.14 d	127.04 d	125.63 d								
15a	144.33 s	127.90 d	128.37 d	127.90 d	28.57 d	15.35 t										
15b	141.22 s	124.89 d	129.06 d	135.04 s	21.04 q	28.13 d	15.52 t									

* The following signals are also present, δ : 128.67 (d, C-17); 19.16 (q, C-18).

***p*-(1,4-Dideutero-*sec*-butyl)toluene (12b)**, b.p. 64–65 °C (6 Torr), n_D^{20} 1.4938. IR, ν/cm^{-1} : 700, 1470, 1550, 1600, 1880, 1950, 2160 (νCD), 3032, 3068. ^1H NMR, δ : 0.88 (t, 2 H, CH_2D , $J = 7.3$ Hz); 1.26 (s, 3 H, CH_3Ph), 1.28 (d, 2 H, CH_2D , $J = 7.2$ Hz), 1.45–1.75 (m, 2 H, CH_2); 2.50–2.73 (m, 1 H, CHPh); 6.09–7.28 (m, 4 H, CH arom.). MS, m/z : 150 $[\text{M}]^+$. Found (%): C, 79.87; H, 11.97. $\text{C}_{11}\text{H}_{14}\text{D}_2$. Calculated (%): C, 88.00; H, 9.33; D, 2.67.

1,3-Diphenyl-1,4-dideuterobutane (13a), b.p. 138 °C (4 Torr), n_D^{21} 1.5520. IR, ν/cm^{-1} : 715, 810, 840, 1210, 1245, 1373, 1500, 1610, 2160 (νCD), 3040, 3075. ^1H NMR, δ : 1.19 (d, 2 H, CH_2D , $J = 6.8$ Hz); 1.68–1.97 (m, 2 H, CH_2); 2.13–2.79 (m, 2 H, CHPh , CHDPh); 6.72–7.42 (m, 10 H, CH arom.). Found (%): C, 90.48; H, 9.37. $\text{C}_{16}\text{H}_{16}\text{D}_2$. Calculated (%): C, 90.56; H, 7.55; D, 1.89.

1,3-Di(*p*-tolyl)-1,4-dideuterobutane (13b), b.p. 158–159 °C (2 Torr). IR, ν/cm^{-1} : 720, 800, 900, 1020, 1450, 1505, 2150 (νCD), 2850, 2910, 2950. ^1H NMR, δ : 1.19 (d, 2 H, CH_2D , $J = 7.2$ Hz); 1.76–1.90 (m, 2 H, CH_2); 2.18 (s, 6 H, CH_3Ph); 2.34–2.68 (m, 2 H, CH, CHD); 6.83–7.41 (m, 8 H, CH arom.). Found (%): C, 89.91; H, 9.93. $\text{C}_{18}\text{H}_{20}\text{D}_2$. Calculated (%): C, 90.00; H, 8.33; D, 1.67.

1,4-Diphenyl-1,4-dideuterobutane (14a), b.p. 146–147 °C (2 Torr). IR, ν/cm^{-1} : 720, 1620, 2160 (νCD), 3050, 3080. ^1H NMR, δ : 1.68–1.96 (m, 4 H, CHD); 2.35–2.54 (m, 2 H, CHD); 6.83–7.41 (m, 10 H, CH arom.). Found (%): C, 90.45; H, 9.39. $\text{C}_{16}\text{H}_{16}\text{D}_2$. Calculated (%): C, 90.56; H, 7.55; D, 1.89.

1,2-Dideuteroethylbenzene (15a), b.p. 134–135 °C, n_D^{20} 1.4959. IR, ν/cm^{-1} : 690, 730, 1020, 1450, 1500, 1600, 2170 (νCD), 2850, 2970, 3020. ^1H NMR, δ : 1.16 (d, 2 H, CH_2D , $J = 7.6$ Hz); 2.57 (t, 1 H, CH_2 , $J = 7.6$ Hz); 7.02–7.24 (m, 5 H, CH arom.). MS, m/z : 108 $[\text{M}]^+$. Found (%): C, 88.82; H, 11.06. $\text{C}_8\text{H}_8\text{D}_2$. Calculated (%): C, 88.89; H, 7.41; D, 3.70.

***p*-(1,2-Dideuteroethyl)toluene (15b)**, b.p. 61–62 °C (20 Torr), n_D^{20} 1.4950. IR, ν/cm^{-1} : 710, 800, 1010, 1050, 1380, 1450, 1500, 1600, 2170 (νCD), 2420, 2860, 2940, 3030. ^1H NMR, δ : 1.18 (d, 2 H, CH_2D , $J = 7.5$ Hz); 2.25 (s, 3 H, CH_3Ph); 2.54 (t, 1 H, CHD, $J = 7.5$ Hz); 7.02–7.24 (m, 5 H, CH arom.). MS, m/z : 122 $[\text{M}]^+$. Found (%): C, 88.44; H, 11.48. $\text{C}_9\text{H}_{10}\text{D}_2$. Calculated (%): C, 88.52; H, 8.20; D, 3.28.

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