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Transformations of cycloalkanes under the action of organoaluminum compounds and transition metal complexes in the presence of polychloromethanes

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A catalytic system comprising an organoaluminum compound, polychloromethane, and a transition metal complex transforms cyclohexane into dimethyldecalins, cyclooctane into dimethyl- and ethylcyclohexanes, and *endo*-tricyclo[5.2.1.0^{2,6}]decane into its *exo*-isomer under mild conditions.

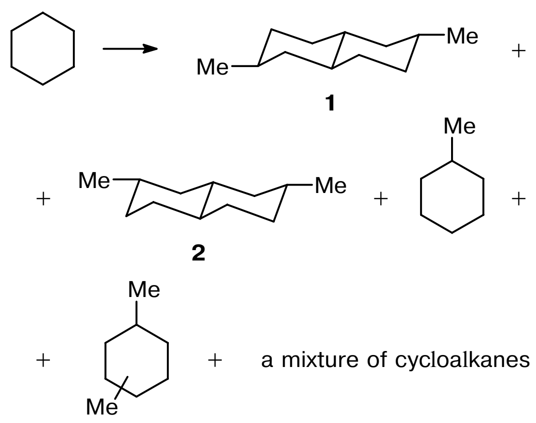
Key words: cyclohexane, cyclooctane, tricyclanes, decalins, catalytic isomerization, organoaluminum compounds, polychloromethanes, catalysis, transition metal complexes.

A search for new systems for skeletal reconstruction of cycloalkanes under mild conditions is a topical problem of modern chemistry.[1] In the present work, the transformations of cyclohexane, cyclooctane, and *endo*-tricyclo[5.2.1.0^{2,6}]decane under rather mild conditions in the presence of a catalytic system comprising organoaluminum compounds (OAC) ($\mathrm{Et_3Al}$, $\mathrm{Bu^i{}_3Al}$, $\mathrm{Bu^i{}_2AlH}$, $\mathrm{Et_2AlCl}$, $\mathrm{EtAlCl_2}$), polychloromethanes ($\mathrm{CCl_4}$ or $\mathrm{CHCl_3}$), and transition metal complexes ($\mathrm{Pd(acac)_2}$, $\mathrm{PdCl_2}$, $\mathrm{Ni(acac)_2}$, $\mathrm{Fe(acac)_3}$, $\mathrm{Co(acac)_3}$, $\mathrm{Cp_2TiCl_2}$) are reported.

Results and Discussion

The degree of conversion of cyclohexane varies from 62 to 94% depending on the composition of the system and the reaction temperature (Table 1). According to GLC/MS data, the main transformation products are dimethyldecalin isomers (32—58 mol.% with respect to cyclohexane consumed). In addition, the reaction yields methylcyclohexane and dimethylcyclohexanes (up to 10%), a complex mixture of unidentified cycloalkanes (up to 30%) probably including tricyclic ones (GLC/MS data), $\mathrm{CH_2Cl_2}$ (~1%), $\mathrm{CHCl_3}$ (~6%), $\mathrm{C_2Cl_6}$ (~1%), and $\mathrm{C_2Cl_4}$ (trace amounts) (Scheme 1).

Scheme 1



Analysis of ^{13}C NMR spectra and GLC/MS data showed that a set of compounds with molecular mass 166 corresponding to dimethyldecalin isomers (dimethylbicyclo[4.4.0]decane), which were isolated by preparative GLC, includes *trans*-3,8-dimethyl-*trans*-bicyclo[4.4.0]decane (**1**, 49%), *trans*-3,9-dimethyl-*trans*-bicyclo[4.4.0]decane (**2**, 38%), and unidentified compounds. The structures of the major isomers **1** and **2** were determined by comparing their ^{13}C NMR spectra with the known data[2] and correlate with the fact[3] that these are the most stable isomers in an equilibrium mixture of dimethylbicyclo[4.4.0]decanes.

Under mild conditions, these bicyclanes are formed from cyclohexane in up to 22% yield under the action of a superelectrophilic system $\mathrm{MeCOCl{-}2AlBr_3}$,[4] from cyclopentane in up to 27% yield under the action of $\mathrm{CBr_4{-}2AlBr_3}$,[5] and from methylcyclopentane and cyclohexane in up to 9% yield under the action of a system comprising polyhalogenomethanes ($\mathrm{CBr_4}$, $\mathrm{CCl_4}$, or $\mathrm{CHCl_3}$) and aluminum halides ($\mathrm{AlBr_3}$ or $\mathrm{AlCl_3}$).[6] In our case, the degree of conversion of cyclohexane and the yields of bicyclanes are much higher.

Transformation of cyclooctane in the presence of a $\mathrm{Bu^i{}_2AlH{-}CCl_4{-}PdCl_2}$ system (6 : 40 : 0.1 per 100 parts

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Table 1. Conversion of cyclohexane under the action of different OAC—CCl_4—M catalytic systems and the yield of dimethyl[4.4.0]decane

OAC	Catalyst (M)	Molar ratio C_6H_{12} : OAC : CCl_4 : M	T/°C	t/h	Conversion of C_6H_{12}	Yield of $C_{12}H_{22}$
					%	
$Bu^i{}_2AlH$	$Pd(acac)_2$	100 : 10 : 50 : 0.1	12	6	83	38
Et_3Al	$Pd(acac)_2$	100 : 12 : 34 : 0.1	20	6	76	40
Et_3Al	$Pd(acac)_2$	100 : 13 : 27 : 0.1	15	24	79	32
Et_3Al	Cp_2TiCl_2	100 : 13 : 45 : 0.1	60	0.25	62	33
Et_3Al	$Co(acac)_3$	100 : 9 : 32 : 0.1	81	1	94	33
Et_3Al	$Fe(acac)_3$	100 : 9 : 32 : 0.1	81	1	73	32
Et_3Al	$Ni(acac)_2$	100 : 9 : 32 : 0.1	81	0.2	79	43
Et_3Al	$Pd(acac)_2$	100 : 19 : 32 : 0.1	81	0.25	45	25
Et_3Al	$Pd(acac)_2$	100 : 5 : 32 : 0.1	81	4	10	30
Et_3Al	$Pd(acac)_2$	100 : 9 : 16 : 0.1	81	0.5	63	37
Et_3Al	$Pd(acac)_2$	100 : 9 : 8 : 0.1	81	4	63	22
Et_3Al	$Pd(acac)_2$	100 : 9 : 48 : 0.1	81	1	79	41
Et_3Al*	$Pd(acac)_2$	100 : 9 : 27 : 0.1	81	1.5	81	58
Et_3Al**	$Pd(acac)_2$	100 : 9 : 48 : 0.1	81	3	52	35
Et_3Al	$PdCl_2$	100 : 9 : 32 : 0.1	81	0.25	86	39
Et_3Al*	$Ni(acac)_2$	100 : 9 : 32 : 0.1	81	2	54	36
$Bu^i{}_3Al$	$PdCl_2$	100 : 5 : 32 : 0.1	81	0.5	71	31
Et_2AlCl	$PdCl_2$	100 : 4 : 32 : 0.1	20	0.25	78	43
$EtAlCl_2$	$PdCl_2$	100 : 10 : 32 : 0.1	20	0.1	76	36
Et_3Al	$PdCl_2$	100 : 9 : 32 : 0.1	20	0.5	83	38

* With $CHCl_3$ instead of CCl_4.

** With CH_2Cl_2 instead of CCl_4.

of C_8H_{16}) gives ethylcyclohexane (43%) and a mixture of four dimethylcyclohexane isomers (57%) in a 77% overall yield (Scheme 2). Dimethylcyclohexane isomers isolated by preparative GLC were identified by comparing their ^{13}C NMR spectra with the known data.[7] With Et_3Al instead of $Bu^i{}_2AlH$ and the same ratio of the starting reagents, no ethylcyclohexane is formed, the only products being dimethylcyclohexane isomers.

Scheme 2

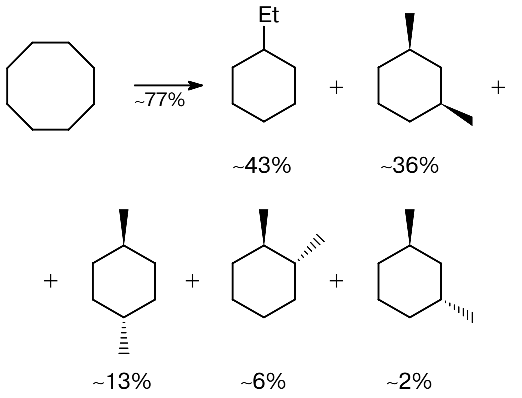


Table 2. Isomerization of *endo*-tricyclo[5.2.1.$0^{2,6}$]decane in different OAC—CCl_4—M catalytic systems

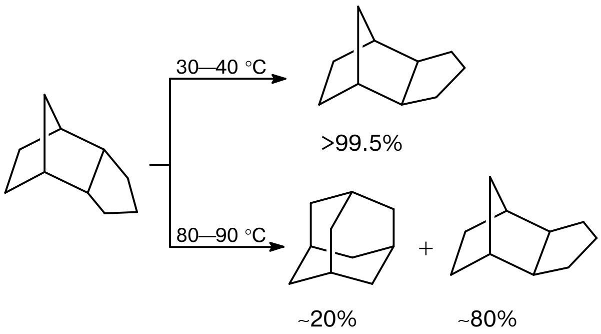
OAC	Catalyst (M)	T/°C	t /min	Yield of *exo*-isomer (%)
$Bu^i{}_2AlH$	$PdCl_2$	12	40	99
Et_3Al	$Pd(acac)_2$	10	45	98
Et_3Al*	$Pd(acac)_2$	40	60	99
Et_3Al	$Ni(acac)_2$	20	50	98
$Bu^i{}_3Al$	$PdCl_2$	40	60	99
Et_2AlCl	$PdCl_2$	20	30	97
$EtAlCl_2$	$PdCl_2$	20	15	97

* With $CHCl_3$ instead of CCl_4.

endo-Tricyclo[5.2.1.$0^{2,6}$]decane in pentane at 10—40 °C isomerizes into *exo*-tricyclo[5.2.1.$0^{2,6}$]decane (Table 2), while its heating in octane at 80—90 °C affords a mixture of the *exo*-isomer with adamantane (Scheme 3). A chromatogram of the reaction products contains a peak that coincides with the peak for authentic adamantane. The ^{13}C NMR spectrum of tricyclodecane shows not only signals for the major *exo*-isomer but also signals at δ 38.02 (38.0) and 28.65 (28.6) characteristic of adamantane (the literature data[2] are given in parentheses). The formation of adamantane was also confirmed by GLC/MS data. The results obtained with different OACs and transition metal complexes are summarized in Table 2. Similar transformations of the *endo*-isomer catalyzed by aluminum chloride occur under more drastic conditions.[8]

The transformations observed of cycloalkanes are probably due to a superelectrophilic effect of a complex

Scheme 3



of polyhalogenomethane with aluminum chloride,[6] which is formed in the reaction of OAC with polyhalogenomethane in the presence of transition metal complexes as catalysts.[9] However, considering that the degree of conversion of cyclohexane and the yields of the reaction products are significantly higher than those observed with other electrophilic catalytic systems, one cannot exclude the process involves reduced forms of transition metals.

Experimental

Reagent grade CCl_4, $CHCl_3$, and cyclohexane were used without additional purification. Et_3Al (91%), $Bu^i{}_3Al$ (91%), $Bu^i{}_2AlH$ (73%), Et_2AlCl (90%), and $EtAlCl_2$ (86%) were commercial chemicals. Cyclooctane and *endo*-tricyclo[5.2.1.0^{2,6}]decane were prepared by hydrogenation of cyclooctadiene and the cyclopentadiene dimer, respectively, over a nickel catalyst.[10] ^{13}C NMR spectra were recorded on a JEOL-FX90Q spectrometer. The reaction mixtures were analyzed by GLC on a Chrom-5 chromatograph with a capillary column (25 m; 5% SE-30) and on a Finnigan-4021 GLC/MS instrument. Identification of compounds was performed with the use of a database stored in the instrument′s computer. The reaction products were separated on a Carlo Erba preparative chromatograph.

Transformations of cyclohexane. Carbon tetrachloride (8 mL, 83 mmol) was added dropwise in an atmosphere of argon at ≤10 °C to a mixture of cyclohexane (26 mL, 241 mmol), $Pd(acac)_2$ (78.5 mg, 0.256 mmol), and 5 mL of 91% Et_3Al (30 mmol). Addition of CCl_4 was accompanied by the evolution of ethane and ethylene. The reaction mixture was stirred at 10—12 °C for 3 h until HCl ceased to evolve. When the reaction was completed, two layers were formed. The upper layer was withdrawn and passed through Al_2O_3. GLC analysis of the reaction products (20.3 g) showed that the content of dimethyldecalins is 30% and that of the non-consumed cyclohexane is 24%. Fractional distillation with a distilling column at 200—220 °C gave a liquid (4.5 g) containing isomer **1** (49%), isomer **2** (38%), four unidentified dimethyldecalin isomers with M = 166 (each 2—3%), and five isomers with M = 166 (each 0.2—0.3 %).

Compound 1. ^{13}C NMR ($CDCl_3$), δ (the literature data[2] are given in parentheses): 43.0 (43.0) (C(1), C(2), C(6), C(7)); 33.1 (33.1) (C(3), C(8)); 35.6 (35.6) (C(4), C(9)); 34.3 (34.2) (C(5), C(10)); 22.8 (22.8) (C(3)CH_3, C(8)CH_3). M = 166.

Compound 2. ^{13}C NMR ($CDCl_3$), δ (the literature data[2] are given in parentheses): 43.3 (43.3) (C(1), C(2), C(10)); 33.1 (33.1) (C(3), C(9)); 35.7 (35.7) (C(4), C(8)); 34.0 (34.0) (C(5), C(7)); 42.9 (42.9) (C(6)); 22.9 (22.8) ((C(3)CH_3, C(9)CH_3). M = 166.

The reaction of cyclooctane with $Bu^i{}_3Al—CCl_4—PdCl_2$. Palladium dichloride (10.8 mg), cyclooctane (5 mL), and $Bu^i{}_2AlH$ (1 mL) were placed in a three-neck round-bottom flask equipped with a magnetic stirrer and a reflux condenser. Then, a mixture of CCl_4 (2 mL) and cyclooctane (2 mL) was added dropwise at 8—10 °C. The reaction mixture was slowly heated to 50 °C with continuous stirring. The evolution of HCl started at ~40 °C and lasted for 2 h. After the reaction was completed, the reaction mixture separated into two layers. The upper layer was withdrawn and passed through Al_2O_3. Ethylcyclohexane and dimethylcyclohexane isomers were isolated by preparative GLC. Ethylcyclohexane, ^{13}C NMR ($CDCl_3$), δ: 39.7 (C(1)); 33.2 (C(2), C(6)); 26.6 (C(3), C(5)); 26.9 (C(4)). The mixture of dimethylcyclohexane isomers contained *cis*-1,3-dimethylcyclohexane (63%), *trans*-1,4-dimethylcyclohexane (22%), *trans*-1,2-dimethylcyclohexane (11%), and *trans*-1,3-dimethylcyclohexane (2%).

***cis*-1,3-Dimethylcyclohexane.** ^{13}C NMR, δ (the literature data[7] are given in parentheses): 33.1 (32.85) (C(1), C(3)); 44.8 (44.70) (C(2)); 35.4 (35.40) (C(4), C(6)); 26.7 (26.45) (C(5)); 22.7 (22.85) (C(1)CH_3, C(3)CH_3).

***trans*-1,4-Dimethylcyclohexane.** ^{13}C NMR, δ (the literature data[7] are given in parentheses): 32.8 (32.70) (C(1), C(4)); 35.7 (35.65) (C(2), C(3), C(5), C(6)); 22.9 (22.70) (C(1)CH_3, C(4)CH_3).

***trans*-1,2-Dimethylcyclohexane.** ^{13}C NMR, δ (the literature data[7] are given in parentheses): 39.6 (39.55) (C(1), C(2)); 36.1 (36.05) (C(3), C(6)); 27.1 (26.85) (C(4), C(5)); 20.6 (20.25) (C(1)CH_3, C(2)CH_3).

***trans*-1,3-Dimethylcyclohexane.** ^{13}C NMR, δ (the literature data[7] are given in parentheses): 27.1 (27.05) (C(1), C(3)); 41.5 (41.45) (C(2)); 34.0 (33.90) (C(4)); 20.9 (20.75) (C(5)); 32.9 (32.90) (C(6)); 20.6 (20.50) (C(1)CH_3, C(3)CH_3).

The reaction of *endo*-tricyclo[5.2.1.0^{2,6}]decane with $Bu^i{}_3Al—CCl_4—PdCl_2$. To a stirred mixture of pentane (6 mL), *endo*-tricyclo[5.2.1.0^{2,6}]decane (1.324 g), $PdCl_2$ (10.8 mg), and diisobutylaluminum hydride (1 mL), a mixture of CCl_4 (2 mL) and pentane (2 mL) was added dropwise at 10—12 °C in an atmosphere of Ar. After 40 min, the reaction mixture separated into two layers. The upper layer was withdrawn and passed through Al_2O_3. The resulting transparent liquid contained *exo*-tricyclo[5.2.1.0^{2,6}]decane (99.5%). The content was determined by GLC using the method of an internal standard.

The *exo*-isomer, ^{13}C NMR ($CDCl_3$), δ: 48.4 (C(1), C(7)); 40.9 (C(2), C(6)); 29.0 (C(3), C(5)); 27.5 (C(4)); 32.7 (C(8), C(9)); 32.1 (C(10)). The starting *endo*-isomer, ^{13}C NMR, δ: 45.8 (C(1), C(7)); 41.9 (C(2), C(6)); 27.2 (C(3), C(5)); 29.0 (C(4)); 23.3 (C(8), C(9)); 43.5 (C(10)).

References

1. A. E. Shilov and G. B. Shul′pin, *Aktivatsiya i kataliticheskie reaktsii uglevodorodov* [*Activation and Catalytic Reactions of Hydrocarbons*], Nauka, Moscow, 1995, 398 pp. (in Russian).
2. J. K. Whitesell and M. A. Minton, *Stereochemical Analysis of Alicyclic Compounds by C^{13} NMR Spectroscopy*, Chapman and Hall, London—New York, 1987, p. 231.

3. S. S. Berman and L. N. Stukanova, *Neftekhimiya*, 1970, **10**, 635 [*Petroleum Chemistry*, 1970, **10** (Engl. Transl.)].
4. I. S. Akhrem, A. V. Orlinkov, E. I. Mysov, and M. E. Vol´pin, *Tetrahedron Lett.*, 1981, **22**, 3891.
5. I. S. Akhrem, S. V. Vitt, I. M. Churilova, and A. V. Orlinkov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 2304 [*Russ. Chem. Bull.*, 1999, **48**, 2279 (Engl. Transl.)].
6. I. S. Akhrem, I. M. Churilova, and S. V. Vitt, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 78 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 81].
7. E. Breit-Maier and W. Voelter, *^{13}C NMR Spectroscopy. Methods and Applications*, Verlag Chemie, Weinheim, 1974, p. 276.
8. US Pat. 4 270 014, 1981.
9. R. A. Sadykov and I. Kh. Teregulov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1580 [*Russ. Chem. Bull.*, 1998, **47**, 1537 (Engl. Transl.)]; R. A. Sadykov and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1003 [*Russ. Chem. Bull.*, 1999, **48**, 995 (Engl. Transl.)].
10. P. I. Kutuzov, Yu. P. Bazhenov, R. I. Khusnutdinov, I. A. Shchadneva, B. I. Kutepov, A. I. Khazipova, L. Z. Kas´yanova, and U. M. Dzhemilev, *Abstrs., IV Rossiiskaya konferentsiya s uchastiem stran SNG "Nauchnye osnovy prigotovleniya katalizatorov"* [*IV Russian Conf. with the Participation of the Countries from the Commonwealth of the Independent States "Scientific Grounds of Catalyst Preparation"*], Sterlitamak, 2000, UD-11, 204.

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