Synthesis and transformations of metallocycles
13.* Stereoselective transformation of *trans*-3,4-dialkylalumacyclopentanes to *trans*-3,4-dialkylcyclobutanes

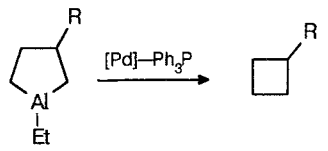
U. M. Dzhemilev, A. G. Ibragimov, M. N. Azhgaliev, A. P. Zolotarev, and R. R. Muslukhov*

Institute of Organic Chemistry, Ural Branch of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Ftderation. Fax: +7 (347) 237 2914

A novel preparative method for synthesizing *trans*-1,2-dialkylcyclobutanes from alumacyclopentanes using palladium phosphine complexes as catalysts has been developed.

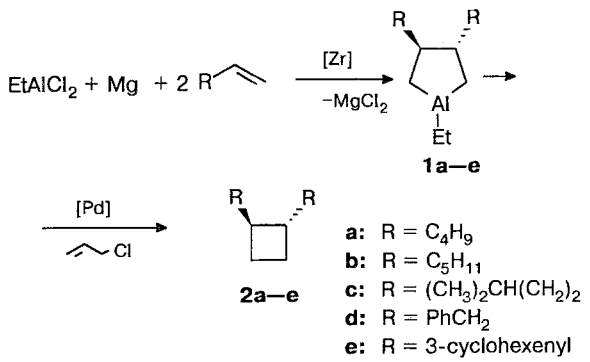
Key words: synthesis, selective transformation, cyclobutanes.

Monoalkyl substituted alumacyclopentanes (ACP) are transformed by the action of palladium catalysts to alkylcyclobutanes[2] according to the scheme:



In a continuation of the investigations in this field into the elaboration of a stereoselective synthesis of 1,2-dialkylcyclobutanes (CB) we studied the transformations of *trans*-3,4-dialkyl-ACP[3] by the above scheme. The starting ACP **1a—e** were obtained by cycloalumination of 1-hexene, 1-heptene, 5-methyl-1-hexene, allylbenzene, and 4-vinylcyclohexene with $EtAlCl_2$, metallic Mg, and catalytic amounts of Cp_2ZrCl_2.[3]

The treatment of the above ACP with a threefold excess of allyl chloride in the presence of 5 mol. % of Pd complexes resulted in *trans*-1,2-dialkylcyclobutanes **2a—e**.



Among the tested catalytic systems based on Pd, Ni, Fe, Co, Rh, and Cu complexes and allyl compounds (allyl halides; diallyl, butyl allyl, and phenyl allyl ethers, triallylamine) employed as reoxidants, the largest yields of CB (65—75 %) were obtained using allyl chloride and catalytic amounts (5 mol. %) of the $Pd(acac)_2 \cdot 2Ph_3P$ complex.

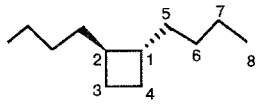
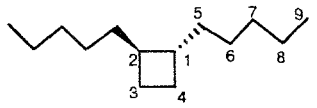
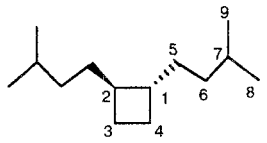
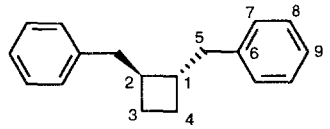
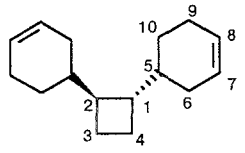
It can be assumed that cyclobutanes **2a—e** have the *trans*-configuration if their formation from ACP **1a—e** (*cf.* Ref. 4) does not change the configuration of the chiral centers. The structure of compounds **2a—e** was confirmed by analyzing their ^{13}C NMR spectra. First of all, the number of signals in the spectra (Table 1) is two times less than the number of carbon atoms, which indicates that the molecule has a symmetry axis.

The positions of the alkyl substituents in the cyclobutane ring was established by additive calculations. For example, based on the known spectral parameters for cyclobutane (δ 23.3, $^1J_{CH}$ = 134 Hz),[5] and monoalkylcyclobutanes,[2] in particular, methylcyclobutane,[6] the parameters of the additive effect of alkyl substituents on the chemical shifts of the carbon atoms in the cyclobutane ring were determined, and spectra were calculated for the two possible variants of substitution: 1,2-dibutylcyclobutane (δC(1),C(2) = 41.6, δC(3),C(4) = 23.8) and 1,3-dibutylcyclobutane (δC(1),C(3) = 31.5, δC(2),C(4) = 22.9). Since the difference between 1,2- and 1,3-substitution is so significant (10 ppm), the similar chemical shifts in the calculated and experimental spectra clearly indicate 1,2-disubstitition in dibutylcyclobutane **2a**. The significant differences in the chemical shifts for the C(5) and C(5′) atoms in the *trans*- and *cis*-isomers of **2a** are due to the contribution of 1,2-*cis* steric interaction. For example, the chemical shifts of the methyl groups in the ^{13}C NMR spectra of methylcyclohexane and *trans*-1,2-dimethylcyclohexane (*ee*) in the absence of steric interaction coincide, whereas *cis*-interaction results in a

* For communication 12, *cf.* Ref. 1.

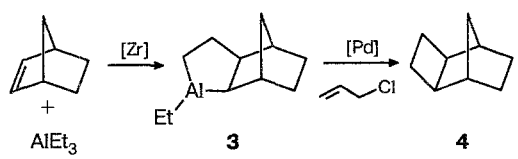
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 273—275, February, 1994.

Table 1. Chemical shifts (δ) and multiplicity of signals in ^{13}C NMR spectra of disubstituted cyclobutanes

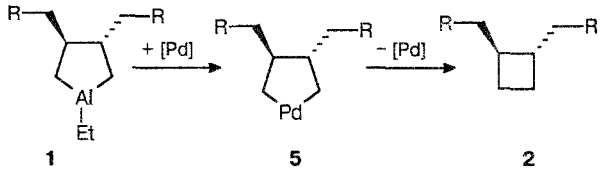
Compound	C(4)	C(1)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
2a 	24.91 t (134.8)	42.61 d (128.4)	36.50 t (124.2)	29.73 t	22.93 t	14.17 q		
2b 	24.97 t	42.61 d	36.76 t	27.13 t	32.16 t	22.70 t	14.17 q	
2c 	24.84 t	42.74 d	36.63 t	34.46 t	28.08 d	22.62 q	22.62 q	
2d 	24.97 t	43.30 d	42.13 t	140.99 c	128.65 d	128.17 d	125.65 d	
2e 	21.32 t	44.60 d	39.10 d	28.43 t	127.10 d	126.74 d	25.48 t	26.70 t

4.3 ppm upfield shift of the signals for the methyl groups in the spectrum of *cis*-1,2-dimethylcyclohexane (*ea*).[6] In the case of *cis* orientation of the butyl groups in compound **2a**, a similar contribution to shielding would cause significant upfield shifts for the C(5) and C(5′) atoms in comparison to that for the C(5) atom in butylcyclobutane.[2] The chemical shifts for the C(5) and C(5′) atoms (δC(5),C(5′) = 36.5) are practically equal to those for C(5) in monoalkylcyclobutanes, *e.g.*, butylcyclobutane (δ = 36.8), and indicate the absence of steric interactions of the butyl groups in compound **2a**, and thus the alkyl substituents in **2a** have the *trans* orientation.

The reaction elaborated by us has general applicability and can involve cyclic and polycyclic alumacyclopentanes obtained by catalytic cycloalumination of compounds of the norbornene series with $AlEt_3$ (*cf.* Ref. 8). For example, the treatment of 3-ethyl-3-alumatricyclo[5.2.1.$0^{2,6}$]decane (**3**) with excess allyl chloride under the conditions described above results in *exo*-tricyclo[4.2.1.$0^{2,5}$]nonane (**4**) in 68 % yield. This makes it possible to synthesize polycyclic hydrocarbons.



It may be assumed[9] that the formation of disubstituted cyclobutanes involves palladacyclopentane intermediates **5** according to the following scheme:



The above transformations of ACP under the action of catalytic amounts of palladium phosphine complexes combined with allyl chloride provide a new approach to the regio- and stereoselective synthesis of *trans*-1,2-disubstituted cyclobutanes, which were difficult to obtain, from olefins using complex Zr- and Pd-containing catalysts.

Experimental

Cycloalumination[3] was carried out under dry argon. GLC analyses of the resulting substituted cyclobutanes were performed on a Khrom-5 chromatograph with He as the carrier gas, 1200×3 mm column, 5 % SE-30 or 15 % PEG-6000 on Chromaton N-AW. IR spectra were recorded in films on a UR-20 spectrophotometer. Mass spectra were obtained on an

MX-1300 spectrometer, temperature of the feed vessel 100 °C, energy of ionizing electrons 70 and 12 eV. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Tesla BS-567 spectrometer (100 MHz). ^{13}C NMR spectra were obtained on a Jeol-90Q spectrometer (22.5 MHz) using TMS as the internal standard.

Synthesis of *trans*-1,2-dialkylcyclobutanes. Cp_2ZrCl_2 (87.6 mg, 0.3 mmol), Mg powder (240 mg, 10 mg-at.), 1-heptene (1.96 g, 20 mmol), THF (10 mL), and $EtAlCl_2$ (1.27 g, 10 mmol) were placed at −5÷0 °C into a 50-mL glass reactor. The temperature was slowly increased to 23—25 °C, and the mixture was stirred for 10 h on a magnetic stirrer. Allyl chloride (30 mmol) and a catalyst consisting of $Pd(acac)_2$ (0.5 mmol) and Ph_3P (1 mmol) were added at −5 °C to the organoaluminum compound obtained. The temperature was adjusted to ~20 °C, and the mixture was stirred for 10 h. The reaction was accompanied by the formation of an equimolar amount of propene. The reaction mixture was treated with 5 % HCl, and the product was extracted with ether and isolated by distillation *in vacuo* or by column chromatography (silica gel L, 40/100 μ). The purity of the products obtained was 95—98 %.

***trans*-1,2-Dibutylcyclobutane (2a),** yield 75 %. B.p. 65—67 °C (4 Torr). IR, ν/cm^{-1}: 2970, 2940, 2870, 1470, 1390, 1120, 1080, 750. ^{1}H NMR, δ: 0.88 (t, 6 H, CH_3); 1.11—2.30 (m, 18 H, CH, CH_2). MS, *m/z*: 168 [M$^+$]. Found (%): C, 85.65; H, 14.35. $C_{12}H_{24}$. Calculated (%): C, 85.71; H, 14.29.

***trans*-1,2-Dipentylcyclobutane (2b),** yield 73 %. B.p. 82—83 °C (2 Torr). IR, ν/cm^{-1}: 2970, 2940, 2870, 1475, 1390, 1260, 1230, 1115, 930, 980, 740. ^{1}H NMR, δ: 0.93 (t, 6 H, CH_3); 1.18—2.16 (m, 22 H, CH, CH_2). MS, *m/z*: 196 [M$^+$]. Found (%): C, 85.63; H, 14.37. $C_{14}H_{28}$. Calculated (%): C, 85.71; H, 14.29.

***trans*-1,2-Diisopentylcyclobutane (2c),** yield 69 %. B.p. 73—74 °C (1 Torr). IR, ν/cm^{-1}: 2970, 2930, 2880, 1480, 1395, 1365, 930. ^{1}H NMR, δ: 0.86 (d, 12 H, CH_3); 1.02—2.25 (m, 16 H, CH, CH_2). MS, *m/z*: 196 [M$^+$]. Found (%): C, 85.66; H, 14.34. $C_{14}H_{28}$. Calculated (%): C, 85.71; H, 14.29.

***trans*-1,2-Dibenzylcyclobutane (2d),** yield 60 %. R_f 0.47 (hexane—acetone, 10:3, Silufol). IR, ν/cm^{-1}: 3040, 2955, 1650, 1605, 1500, 1460, 1495, 930, 750. ^{1}H NMR, δ: 1.47—1.96 (m, 6 H, CH, CH_2); 2.50—2.60 (m, 4 H, CH_2—Ph); 7.00—7.40 (m, 10 H, Ph). MS, *m/z*: 236 [M$^+$]. Found (%): C, 91.59; H, 8.41. $C_{18}H_{20}$. Calculated (%): C, 91.53; H, 8.47.

***trans*-1,2-Di(3-cyclohexenyl)cyclobutane (2e),** yield 62 %. B.p. 108—110 °C (1 Torr). IR, ν/cm^{-1}: 3020, 2960, 1670, 1440, 905, 720, 640. ^{1}H NMR, δ: 1.00—2.20 (m, 20 H, CH, CH_2); 5.65 (m, 4 H, CH=CH). MS, *m/z*: 216 [M$^+$]. Found (%): C, 88.82; H, 11.18. $C_{16}H_{24}$. Calculated (%): C, 88.89; H, 11.11.

***exo*-Tricyclo[4.2.1.0^{2,5}]nonane (4).** Yield 68 %. B.p. 52—54 °C (5 Torr), n_D^{20} = 1.4862. IR, ν/cm^{-1}: 2960, 2880, 1475, 1395, 920, 740. ^{1}H NMR, δ: 0.85—1.45, 1.17—1.65, 1.89—2.14 (m, 14 H, CH, CH_2). ^{13}C NMR, δ: 41.82 (d, C-1, C-6); 39.45 (d, C-2, C-5); 31.80 (t, C-a); 23.10 (t, C-3, C-4); 27.67 (t, C-7, C-8). MS, *m/z*: 122 [M$^+$]. Found (%): C, 88.50; H, 11.50. C_9H_{14}. Calculated (%): C, 88.50; H, 11.50.

References

1. R. R. Muslukhov, L. M. Khalilov, A. G. Ibragimov, A. P. Zolotarev, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2742 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 2172 (Engl. Transl.)].
2. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2152 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1981 (Engl. Transl.)].
3. U. M. Dzhemilev, A. G. Ibragimov, A. B. Morozov, R. R. Muslukhov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1607 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1425 (Engl. Transl.)].
4. R. R. Muslukhov, L. M. Khalilov, A. P. Zolotarev, A. B. Morozov, A. G. Ibragimov, U. M. Dzhemilev, and G. A. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2110 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1646 (Engl. Transl.)].
5. H. Günter, *NMR Spectroscopy*, J. Wiley & Sons, Chichester *etc.*, 1980.
6. J. K. Whitell and M. A. Minton, *Stereochemical Analysis of Alicyclic Compounds by C-13 NMR Spectroscopy*, Chapman and Hall Ltd., London, 1987, 12, 38.
7. A. A. Petrov, *Stereokhimiya nasyshchennykh uglevodorodov* [*Stereochemistry of Saturated Hydrocarbons*], Nauka, Moscow, 1981, 254 p. (in Russian).
8. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, L. M. Khalilov, and R. R. Muslukhov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 386 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 300 (Engl. Transl.)].
9. A. Stockis and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 2952.
10. R. R. Muslukhov, L. M. Khalilov, A. G. Ibragimov, A. P. Zolotarev, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2742 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 2172 (Engl. Transl.)].

Received November 10, 1992;
in revised form February 26, 1993