Pergamon

Tetrahedron Letters 39 (1998) 5611–5614

TETRAHEDRON LETTERS

Kinetic resolution of racemic 2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthalene by chiral dimethylaluminum complexes and an achiral Pd catalyst, as well as by achiral dimethylaluminum reagents in the presence of a chiral Pd catalyst

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Received 18 March 1998; accepted 19 May 1998

Abstract

Kinetic resolution of the racemic title compound was shown to take place during its methylation with either $(Me_2AlOCH_2CH_2OMe)_2$ or $Me_2Al(CH_2)_3NMe_2$ in the presence of an optically active Pd(binap) catalyst, as well as during its alkylation with either (*S*)-(+)-$[Me_2AlOCH_2CH(Me)OCH_2Ph]_2$ or (*S*)-(+)-$[Me_2AlOCH_2CH(CH_2CHMe_2)NMe_2]_2$ in the presence of an achiral palladium complex. The ee values of the resolved binaphthyl derivatives by the two methods were up to 69 and 12%, respectively. The latter method represents the first application of a stabilized dialkylaluminum complex with a chiral chelating ligand for asymmetric induction.

Keywords: Alkylation; Aluminum compounds; Asymmetric induction; Palladium compounds

Recently [1] we found that aluminum complexes of the general formula $(Me_2AlX\text{-}Y)_n$

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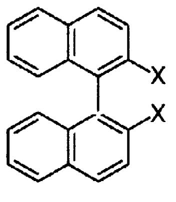
PII: S0040-4039(98)01054-5

(where n = 1,2, X = $(CH_2)_3$, $2\text{-}C_6H_4CH_2$, $8\text{-}C_{10}H_6$, $O(CH_2)_2$, $O\text{-}2\text{-}C_6H_4$, and Y = OMe, NMe_2) cross-methylate various aryl bromides, iodides and triflates [2], in the presence of palladium catalysts, under standard laboratory conditions. We now wish to report the first examples of the application of such stabilized dimethylaluminum complexes for kinetic resolution of a racemic biaryl compound either by utilizing chiral aluminum methylation reagents together with an achiral palladium catalyst, or by employing achiral aluminum compounds in the presence of a chiral palladium complex.



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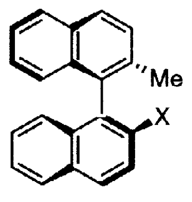

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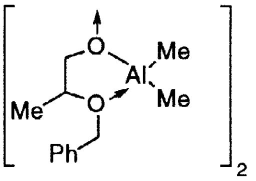

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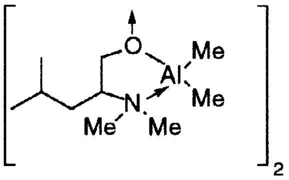

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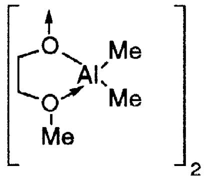

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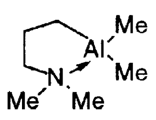

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In a typical experiment a solution of 170 mg (0.31 mmol) of (±)-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthalene [3] (**1**, X = OSO_2CF_3), (±)-Pd(binap)$(OAc)_2$ [prepared *in situ* from 2.7 mg (0.0123 mmol) of $Pd(OAc)_2$ and 15.4 mg (0.024 mmol) of (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene] in dry benzene was refluxed under Ar for 30 min followed by treatment for 36 h under the same conditions with 138 mg (0.62 mmol) of the chiral aluminum complex (*S*)-(+)-(**3**) (*vide infra*) in 5 ml of the same solvent. Quenching of the reaction mixture with 2% cold aqueous HCl, followed by column chromatography on silica gel (using a 1:9 mixture of hexane and ether as eluent), afforded two distinguishable fractions. The first one (16%) consisted of (*S*)-(-)-2-methyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthalene (**2**, X = OSO_2CF_3) [4] of 12% ee with traces of the corresponding bis-methylated product, **2**, X = Me. This fraction was followed by recovered bis-triflate **1**, X = OSO_2CF_3 (2% ee of (*R*)-(+)-**1**), which was analyzed both by optical rotation measurements (and comparison with pure (*R*)-(+)-**1** of $[\alpha]^{25}_D = 142°$) [3] and by HPLC separation of the mixture on a semi-preparative tris(3,5-dimethylphenyl-carbamate)doped silica column [5,6] using a 2:23 hexane-2-propanol mixtures as eluent at a flow of 1.2 ml/min and 4 kg/cm pressure with a deadtime of 2.0 min. The retention times for the *S*- and *R*-isomers of **1**, X = $OS_2O_2CF_3$ were 13.73 and 14.20 min, respectively.

Replacement of **3** by (*S*)-(+)-(**4**) (*vide infra*) led within 36 h, to 10% resolution of **1**, X = OSO_2CF_3. The methylated product (*S*)-(-)-**2**, X = OSO_2CF_3, so formed, was of 10% ee. When the palladium catalyst (±)-Pd(binap)$(OAc)_2$ was substituted by either $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ (cf., reference [1]) very slow alkylation took place. It might be that the structural similarity between the substrate and the catalyst is an stimulating factor in the asymmetric process.

The two chiral aluminum alkylating agents were prepared by the general methods used for the syntheses of some known stabilized achiral [7] and chiral [8] dimethylaluminum complexes. Compound (*S*)-**3** was obtained as colorless crystals by interaction of equimolar quantities of (*S*)-2-benzyloxy-1-propanol and Me_3Al in pentane at -20-25°C for 12 h.[1]

Compound (*S*)-**4** was obtained as colorless crystals by interaction of equimolar amounts of (*S*)-2-(dimethylamino)-4-methyl-1-pentanol and Me_3Al in ether at -17-25°C for 5 h.[2]

Kinetic resolution of **1**, X = OSO_2CF_3, was achieved also with the aid of the achiral dimethylaluminum complexes (**5**) and (**6**) [9,10] in the presence of a commercially available optically active Pd(binap) catalyst. In the reaction of **1**, X = OSO_2CF_3, [(*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene]palladium (III) dichloride and **5**, 7% of the resolved bis-triflate **1**, and of (*S*)-(-)-**2**, X = OSO_2CF_3 of 42% ee, was obtained within 12

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[1] Mp 86°C; $[\alpha]^{25}_D = +48.1°$ (*c*, 0.02, benzene); ^1H NMR (200 MHz, C_6D_6) δ -0.40 (s, 6H), 0.79 (d, *J* = 6.1 Hz, 3H), 3.25 (m, 2H), 3.58 (m, 1H), 4.36 (d, *J* = 13.4 Hz, 1H), 4.46 (d, *J* = 13.4 Hz, 1H), 7.07-7.17 (m, 5H); ^{13}C NMR (50 MHz, C_6D_6) δ -9.83, 15.00, 64.18, 68.54, 73.00, 128.14, 128.29, 128.66, 137.42; MS (EI, 70 eV, 120°C) *m/z* 429 [$(M\text{-}CH_3)^+$, 91], 371 ($C_{22}H_{32}AlO_3^+$, 3), 323 ($C_{15}H_{25}Al_2O_4^+$, 22), 279 ($C_{13}H_{21}Al_2O_3^+$, 11), 207 ($C_{11}H_{16}AlO_2^+$, 12), 91 ($C_7H_7^+$, 100)]. Found: C, 65.09; H, 8.68. Calc. for $C_{24}H_{38}Al_2O_4$: C, 64.85; H, 8.62%.

[2] Mp 138°C (from pentane); $[\alpha]^{25}_D = +43.3°$ (*C*, 0.03, benzene); ^1H NMR (200 MHz, C_6D_6) δ -0.46 (s, 6H), 0.60 (ddd, J_1 = 13.2 Hz, J_2 = 10.0 Hz, J_3 = 4.3 Hz, 1H), 0.62 (d, J = 6.5 Hz, 3H), 0.67 (d, *J* = 6.5 Hz, 3H), 0.85 (ddd, J_1 = 13.2 Hz, J_2 = 10.0 Hz, J_3 = 2.3 Hz, 1H), 1.09 (m, 1H), 1.85 (s, 6H), 2.85 (m, 1H), 3.20 (d, J_1 = 10.5 Hz, 1H), 3.88 (dd, J_1 = 10.5 Hz, J_2 = 5.8 Hz, 1H); ^{13}C NMR (50 MHz, C_6D_6) δ -10.29, 21.51, 23.99, 25.54, 31.53, 35.00, 42.00, 60.96, 61.66; MS (EI, 70 eV, 80°C) *m/z* 387 [$(M\text{-}CH_3)^+$, 100], 315 ($C_{14}H_{33}Al_2N_2O_2^+$, 19), 323 ($C_9H_{21}AlNO^+$, 54), 128 ($C_8H_{18}N^+$, 68), 114 ($C_7H_{16}N^+$, 51)]. Found: C, 59.46; H, 11.81; N, 7.20. Calc. for $C_{20}H_{48}Al_2N_2O_2$: C, 59.67; H, 12.02; N, 6.96%.

h. Likewise (±)-**1**, X = OSO_2CF_3, (*R*)-(+)-Pd(binap)Cl_2 and **6** furnished after 36 h, 49% of (*S*)-(-)-**2**, X = OSO_2CF_3 of 51% ee. The enantioselectivity could be further increased to 69% ee when the racemic bis-triflate was reacted for 16 h with **6** and (*S*)-(-)-Pd(binap)Cl_2 [or an equimolar mixture of Pd$(OAc)_2$ and (*S*)-(-)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene] until the conversion was 10%.

2,2'-Dibromo-1,1'-binaphthalene (**1**, X = Br) [11] reacted in a similar fashion as **1**, X = OSO_2CF_3, albeit at a lower rate. Since the specific rotation of the dibromo-compound is only ca. 30° [11], monitoring of the kinetic resolution of **1**, X = Br by optical rotation measurements has been found to be inconvenient.

In conclusion, this study has demonstrated that substitution of one Me moiety of Me_3Al by a chiral chelating agent both stabilizes the pyrophoric aluminum compound and generates new asymmetric methylating agents.

We acknowledge the support by the Israel Science Foundation, administered by the Israel Academy for Sciences and Humanities, by the Exchange Program between the Technische Universität, Berlin and the Hebrew University of Jerusalem and by the Deutsche Forschungsgemeinschaft.

References

[1] Blum J, Gelman D, Baidossi W, Shakh E, Rosenfeld A, Aizenshtat Z, Wassermann BC, Frick M, Heymer B, Schutte S, Wernik S, Schumann H. J. Org. Chem. 1997;62: 8681-8688.

[2] Katz J, Schutte S, Michman M, Schumann H, Blum J. Unpublished results.

[3] Vondenhof M, Mattay J. Tetrahedron Lett. 1990;31:985-988.

[4] Hota H, Suzuki T, Miyano S, Inoue Y. J. Mol. Catal. 1989;54:L5-L7.

[5] Okamoto Y, Aburatani R, Fukumoto T, Hatada K. Chem. Lett. 1987;1857-1860.

[6] Okamoto Y, Kaida Y. J. Chromatogr. 1994;666:403-419.

[7] Schumann H, Frick M, Heymer B, Girgsdies F. J. Organomet. Chem. 1996;512:117-126 and references cited therein.

[8] Sierra ML, de Mel VSA, Oliver JP. Organometallics, 1989;8:2486-2488.

[9] Benn R, Rufinska A, Lehmkuhl H, Jannsen E, Krüger C. Angew. Chem. Int. Ed. Engl. 1983;22:779-780.

[10] Pohl L, Hostalek M, Schumann H, Hartmann U, Wassermann W, Brauers A, Regel GK, Hövel R, Balk P, Scholz F. J. Cryst. Growth 1991;107:309-313.

[11] Brown KJ, Berry MS, Murdoch JR. J. Org. Chem. 1985;50:4345-4349.