Journal of Organometallic Chemistry, 105 (1976) 139—143

CATALYSIS OF THE CYCLOADDITION OF 2-PHENYLALLYLMAGNESIUM PHENOXIDE TO *trans*-STILBENE BY MACROCYCLIC COMPLEXING AGENTS AND HEXAMETHYLPHOSPHORAMIDE

GEORGE F. LUTERI and WARREN T. FORD *

Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801 (U.S.A.)

(Received August 19th, 1975)

Summary

2-Phenylallylmagnesium phenoxide and *trans*-stilbene in tetrahydrofuran do not react in 96 h at 25°C, but in the presence of one equivalent of [2.1.1]-cryptate or two equivalents of hexamethylphosphoramide (HMPA) they are completely consumed in <30 min to produce *r*-1, *t*-2, *c*-4-triphenylcyclopentane in 45% and 37% yield respectively. Other macrocyclic polyamines and polyethers also catalyze the reaction, with their order of effectiveness being [2.1.1] cryptate > HMPA > dimethyldiaza-15-crown-5 ≈ 15-crown-5 > dimethyldiaza-18-crown-6 > tetramethylcyclam > 12-crown-4. 18-Crown-6 and tetramethylethylenediamine are catalytically inactive.

Introduction

Complexation of alkali and alkaline earth ions with macrocyclic polyamines and polyethers has been studied extensively since the pioneering work of Pedersen [1-5]. Complexation of cations enables dissolution of metal salts in organic solvents and greatly enhances the reactivities of the anions. Notably absent in these studies has been magnesium ion, probably because its high hydration energy severely limits complexation in aqueous solutions [5]. We have found, however, that macrocyclic polyamines and polyethers are effective catalysts for reaction of an organomagnesium reagent, 2-phenylallylmagnesium phenoxide, in tetrahydrofuran (THF).

* Address correspondence to W.T.F. at Rohm and Haas Company, Research Laboratories, Spring House, Pennsylvania 19477 (U.S.A.)

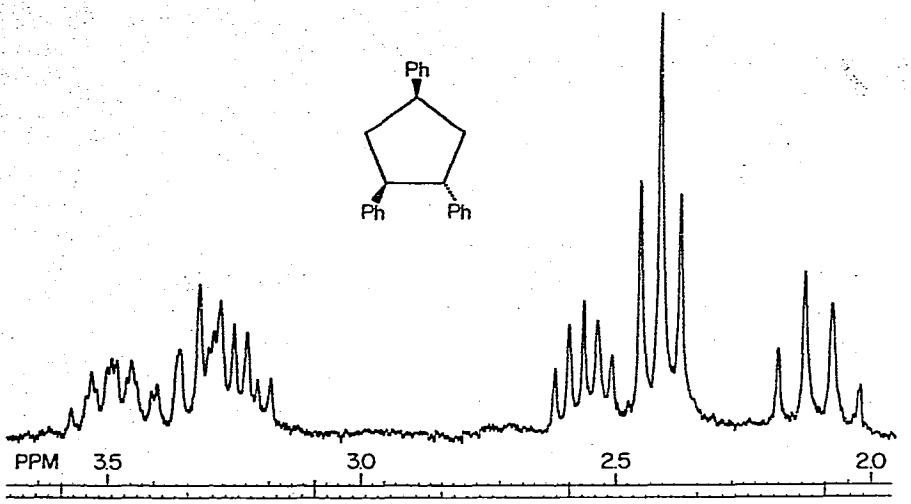


Fig. 1. Aliphatic portion of 220 MHz PMR spectrum of *r*-1, *t*-2, *c*-4-triphenylcyclopentane. Chemical shifts are downfield from TMS.

Results and discussion

Eidenschink and Kauffmann [6] reported that α-methylstyrene, *trans*-stilbene and lithium diisopropylamide (LDIA) in THF produce 1,2,4-triphenylcyclopentane of undetermined configuration in 41% yield after 150 h at 45°C. We have confirmed their results and established the structure as *r*-1, *t*-2, *c*-4-triphenylcyclopentane (I), since its 220 MHz PMR spectrum (Fig. 1) shows five multiplets with relative areas of 1:2:1:2:1. Both of the other possible 1,2,4-triphenylcyclopentane isomers have a plane of symmetry which would give rise to a maximum of four multiplets with relative areas of 2:2:2:1. PMR decoupling experiments and GLPC analyses confirm that the triphenylcyclopentane is a single compound, not an isomeric mixture.

Presumably I is formed by cycloaddition of *trans*-stilbene to a trace of 2-phenylallyllithium, generated by proton transfer from α-methylstyrene to LDIA. In contrast, 2-phenylallylmagnesium phenoxide (II), prepared by magnesium cleavage of 2-phenylallyl phenyl ether [7], in THF fails to react with *trans*-stilbene in 96 h at room temperature. However, complexing agents catalyze the cycloaddition of II and stilbene as shown in Scheme 1 and Table 1. For example, addition of one equivalent of [2.1.1]cryptate [8], whose cavity is the optimum size for complexation of Mg^{2+} [5], to a 0.3 *M* pale yellow solution of II in THF gives a red solution in which the *trans*-stilbene is >97% consumed in <30 min at 25°C. Nearly as effective a catalyst (and 1/2000 as expensive) is hexamethylphosphoramide. Among macrocyclic polyamines and polyethers the 14- and 15-membered crown compounds are active, dimethyldiaza-18-crown-6 and 12-crown-4 are slightly active, and 18-crown-6 and tetramethylethylenediamine (TMEDA) are totally inactive as catalysts.

In any likely stepwise or concerted mechanism for these cycloadditions the triphenylcyclopentyl anion III is an intermediate. (We defer to a later

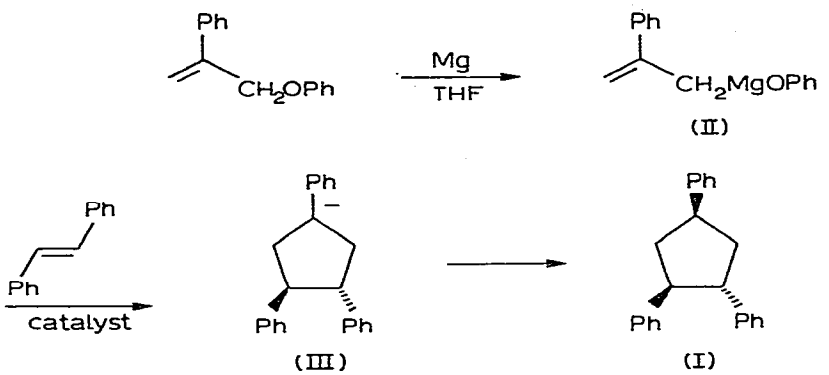
TABLE 1

EFFECTS OF CATALYSTS ON REACTION OF II WITH *trans*-STILBENE[a]

Catalyst	Time for 50% loss of stilbene[b]	Yield of I[c]	
		%	Time (h)
[2.1.1]Cryptate	~0.3 min	45	0.5
HMPA	~0.5 min	37	0.5
Dimethyldiaza-15-crown-5	0.9 min	25	18
15-Crown-5	28 min	30	94
Dimethyldiaza-18-crown-6	140 min	23	18
Tetramethylcyclam[d]	29 min	12	5.0
12-Crown-4	>72 h	7	72

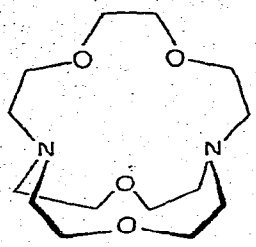
[a] In THF at 25°C with 0.3 *M* II, 0.3 *M* *trans*-stilbene, and 0.3 *M* catalyst (except for HMPA, 0.6 *M*). [b] Time required for disappearance of 50% of the stilbene by GLPC analysis. [c] Maximum % yield of I based on stilbene, and time at which yield was maximized by GLPC analysis. [d] A precipitate of $Mg(OPh)_2$ · tetramethylcyclam formed when catalyst was added to the Grignard solution.

SCHEME 1

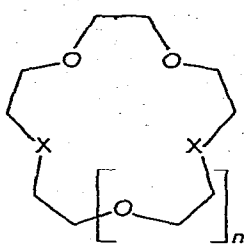


paper our more detailed investigation of the reaction mechanism.) When the course of each reaction listed in Table 1 was followed by GLPC, the yield of I was found to reach a maximum and then decrease slowly with longer reaction time, presumably because anion III reacts further with stilbene, α-methylstyrene, or other unsaturated compounds. The high reactivity of III in the presence of catalysts is also demonstrated by incorporation of only 0.32 atom of deuterium, as determined by mass spectrometry, into I isolated after D_2O hydrolysis of an HMPA-catalyzed reaction mixture. Further, the 220 MHz PMR spectrum of this sample showed the deuterium to be distributed over all three benzylic positions. Anion III must abstract a proton rapidly from either THF or HMPA under the reaction conditions. Uncomplexed benzylic Grignard reagents are not nearly so strongly basic.

Catalysis of the addition of II to *trans*-stilbene is most likely due to conversion of an unreactive 2-phenylallylmagnesium species in THF to more active ionic species by complexation of the magnesium. HMPA effects this conversion nearly as well as [2.1.1]cryptate and better than all of the other macrocyclic complexing agents we have investigated.



[2.1.1] cryptate [8]



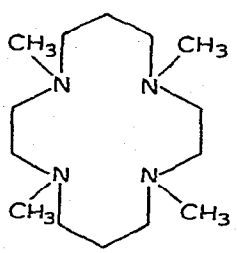
X = O, n = 0: 12-crown-4 [9]

X = O, n = 1: 15-crown-5 [9]

X = O, n = 2: 18-crown-6 [10]

X = NCH_3, n = 1: dimethyldiaza-5-crown-5

X = NCH_3, n = 2: dimethyldiaza-18-crown-6



tetramethylcyclam [11]

Experimental

Materials. 2-Phenylallyl phenyl ether was prepared in two steps from α-methylstyrene by *N*-bromosuccinimide bromination to give 2-phenylallylbromide [12] (lachrymator) followed by treatment of the bromide with phenol and potassium carbonate in acetone [13]. Most of the macrocyclic complexing agents were prepared by literature procedures (noted beside the structures). Dimethyldiaza-15-crown-5 and dimethyldiaza-18-crown-6 were prepared by formaldehyde/formic acid methylation of the corresponding diaza crown compounds [8]. Tetrahydrofuran was freshly distilled from the sodium ketyl of benzophenone. Hexamethylphosphoramide was distilled from calcium hydride under nitrogen at 80 Torr (b.p. 150°C) and stored under nitrogen. *trans*-Stilbene was recrystallized from 95% ethanol: m.p. 124.5-125.1°C (uncorrected).

2-Phenylallylmagnesium phenoxide [7]. A mixture of 3.2 g (0.015 mol) of 2-phenylallyl phenyl ether, 1.0 g (0.045 g-at.) of magnesium turnings and 50 ml of THF was brought to reflux under N_2 in a 100 ml 3-neck flask fitted with a reflux condenser, magnetic stirrer, and N_2 inlet. In order to initiate the reaction 0.2 ml of 1,2-dibromoethane was added. After 3.5 h at reflux, 2-phenylallyl phenyl ether could no longer be detected in the PMR spectrum of the reaction

mixture. The mixture was filtered through a glass wool pad under N_2 to remove the excess magnesium.

r-1, *t*-2, *c*-4-*Triphenylcyclopentane. General procedure.* To the solution of 2-phenylallylmagnesium phenoxide 2.7 g (0.015 mol) of *trans*-stilbene and 0.85 g (0.005 mol) of n-dodecane were added. With magnetic stirring at 25°C under nitrogen either 0.030 mol of HMPA or 0.015 mol of a macrocycle was added, and 5.0 ml aliquots were withdrawn by syringe at various times over a period of hours or days and quenched in aqueous ammonium chloride. Each sample was extracted with hexane, and the organic phase was washed twice with 10% NaOH, twice with 10% HCl, once with saturated $NaHCO_3$ and once with water, and dried over $MgSO_4$. The samples were analyzed by GLPC, programmed from 75 to 285°C at 15°/min, on a glass column of 3.0% SE-30 on 100/120 Gas-Chrom Q at a He flow rate of 40 ml/min. In addition to starting materials with retention times of <8 min, a peak with a retention time of 15 min was observed. GLPC—mass spectrometry showed this peak to have *m/e* 298 for the parent ion, which corresponds to a 1 : 1 adduct of α-methylstyrene and stilbene. Yields were determined by analytical GLPC comparison to the n-dodecane. Samples of this compound were isolated as oils by preparative GLPC on a 6 ft × 0.25 in column of 10% OV-17 on 60-80 Chromosorb W at 290°C. Its 220 MHz PMR spectrum, shown in Fig. 1, corresponds to *r*-1, *c*-2, *t*-4-triphenylcyclopentane.

Acknowledgement

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

1 C.J. Pedersen, J. Amer. Chem. Soc., 89 (1967) 7017.
2 C.J. Pedersen and H.K. Frensdorff, Angew. Chem., Internat. Ed. Engl., 11 (1972) 16.
3 J.J. Christensen, D.T. Eatough and R.M. Izatt, Chem. Rev., 74 (1974) 351.
4 D.J. Cram and J.M. Cram, Science, 183 (1974) 803.
5 J.-M. Lehn, Struct. Bonding, 16 (1973) 1.
6 R. Eidenschink and T. Kauffmann, Angew. Chem., Internat. Ed. Engl., 11 (1972) 292.
7 A. Maercker, J. Organometal. Chem., 18 (1969) 249.
8 B. Dietrich, J.M. Lehn, J.P. Sauvage and J. Blanzat, Tetrahedron, 29 (1973) 1629.
9 J. Dale, G. Borgen and K. Daasvatn, Acta Chem. Scand., B, 28 (1974) 378; F.L. Cook, T.C. Caruso, M.P. Byrne, C.W. Bowers, D.H. Speck and C.L. Liotta, Tetrahedron Lett., (1974) 4029.
10 G.W. Gokel, D.J. Cram, C.L. Liotta, H.P. Harris and F.L. Cook, J. Org. Chem., 39 (1974) 2445.
11 E.K. Barefield and F. Wagner, Inorg. Chem., 12 (1973) 2435.
12 S.F. Reed, Jr., J. Org. Chem., 30 (1965) 3258.
13 V.L. Tweedie and M. Cuscurida, J. Amer. Chem. Soc., 79 (1957) 5466.