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Stereochemistry of palladium-catalyzed telomerization of butadiene with diethylamine

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Abstract

In the telomerization of butadiene with *N,N*-diethylamine catalyzed by palladium acetate, triphenylphosphine, and triethylaluminium, the relative amounts of *E*- and *Z*-octadienyl adducts depend on the Pd/P/Al ratio as well as on the amount of butadiene. Increasing the amount of triethylaluminium favours a high *E/Z* ratio, whereas lower *E/Z* ratios may result when the amount of butadiene is increased. Isomerically pure *N,N*-diethyl-*E*-2,7-octadienylamine can be obtained by use of a catalyst with a Pd/P/Al ratio of 1/1/2.

Introduction

Octadienyl adducts obtained by palladium-catalyzed telomerizations [1] of butadiene with nucleophiles have proved to be useful starting materials for a variety of natural products [2]. It is therefore of interest to find conditions that allow the preparation of isomerically pure adducts. Octadienyl acetates, which are the most commonly used telomers, are prone to undergo palladium-catalyzed rearrangement, and a mixture of two regioisomers (**1** and **2**, Nu = OAc) are obtained [3]. Telomerizations of butadiene with secondary amines, which proceed in high yields under mild conditions, show considerably higher regioselectivity [4]. Since tertiary allylic amines can be conveniently converted into allylic chlorides, acetates, etc., in high yields (with retention of the configuration of the double bond) by standard procedures [5], a large variety of 1-substituted octadienyl adducts are obtainable from *N,N*-diethyl-2,7-octadienylamine.

In synthetic applications the configuration of the internal olefinic bond of the telomers may also be crucial. In the few cases where the *E/Z* ratio of telomers has been determined it has been found to be 96/4 [6] (Nu = OCH_3), 89/11 [7] (Nu = OAc), 95/5 [8] (Nu = OPh) and 86/14 [9] (Nu = SO_2Ph). We have found, however, that the ratios of the isomers can be changed by altering the reaction

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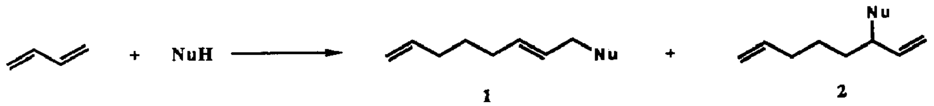

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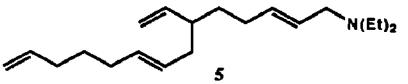

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conditions. A telomerization using a polymer-supported palladium-phosphine complex and triethylaluminium (Pd/Al 1/100, 0.2% Pd) [10*] was shown to yield pure *E*-isomer [5]. This high selectivity was believed to be due to the nature of the polymeric catalyst. However, use of a polymeric palladium catalyst but a higher Pd/Al ratio (1/5, 2% Pd) resulted in an *E*/*Z* ratio of 90/10 [11]. A similar catalytic system (Pd/Al 1/50, 0.15% Pd) used in the telomerization of butadiene and *N*,*N*-diethylamine afforded octadienyl adducts with an *E*/*Z* ratio of > 98/2 (68% yield) [11]. We have now carried out a more detailed study of the factors that influence the configuration of the internal double bond in octadienylamines derived from the palladium-catalyzed telomerization of butadiene and *N*,*N*-diethylamine.

Results and discussion

Reaction of *N*,*N*-diethylamine and butadiene in toluene in the presence of 4 mol% of a catalyst prepared from palladium acetate/triphenylphosphine 1/1 at 40 °C for 18 h afforded a mixture (74%) of *N*,*N*-diethyl-*E*-2,7-octadienylamine (**3**) and *N*,*N*-diethyl-*Z*-2,7-octadienylamine (**4**). It was possible to determine the *E*/*Z* ratio by ^{1}H NMR spectroscopy by integration of the doublets originating from the allylic ($NCH_2CH=$) protons, which were found at δ 3.04 for the *E*-isomer (J 5.5 Hz) and δ 3.10 for the *Z*-isomer (J 5.5 Hz). Under the conditions described this ratio was found to be 96/4 (Table 1, entry 1). Change to a 1/2 or 1/3 palladium/phosphine ratio had no effect on the *E*/*Z* ratio but increased the total yield (entries 2 and 3). No trace of higher telomers was detected in these reactions.

We have previously demonstrated that tertiary allylic amines react with butadiene in the presence of palladium(II), triphenylphosphine, and triethylaluminium to afford telomers formed via cleavage of the carbon–nitrogen bond of the allylic amine and that these telomers may react further with butadiene [5]. Accordingly, telomers **3** and **4** may be expected to undergo further reaction in the presence of triethylaluminium provided an excess of butadiene is present . Table 1, entries 4 and 5, show that higher telomers, probably mainly **5** [12], were indeed formed. The

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* Reference number with asterisk indicates a note in the list of references.

Table 1

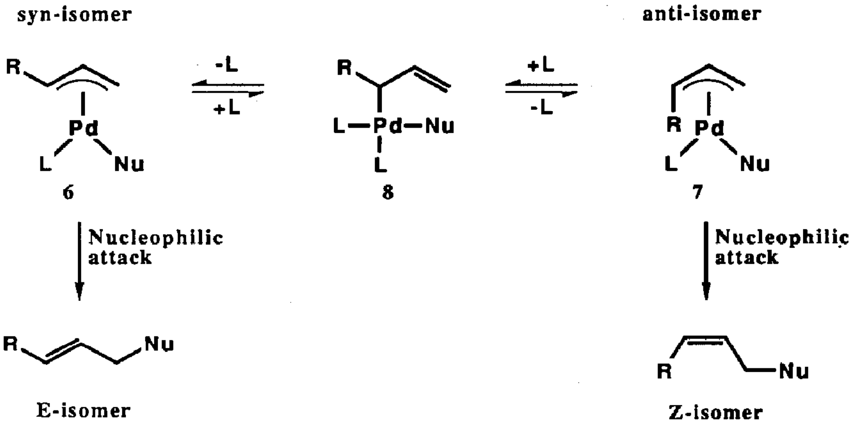
Influence of the catalyst composition on the E/Z ratio of N,N-diethyl-2,7-octadienylamine

Entry	Pd/P/Al	Butadiene/amine	%C_8	%C_{16}	E/Z
1	1/1/0	2.9/1	74	0	96/4
2	1/2/0	2.5/1	93	0	96/4
3	1/3/0	3.5/1	92	0	96/4
4	1/1/1	2.8/1	74	16	92/8
5	1/2/1	3.1/1	85	8	93/7
6	1/1/2	2.7/1	76	14	> 99
7	1/1/2	4.9/1	71	24	> 99
8	1/2/2	2.0/1	75	0	> 99
9	1/2/2	2.5/1	80	8	94/6
10	1/2/2	5.0/1	66	32	96/4
11	1/2/2	5.4/1	56	42	95/5
12	1/3/2	5.1/1	78	0	99/1
13	1/3/2	6.6/1	78	8	98/2

formation of these compounds was somewhat suppressed when the amount of phosphine was increased even at a higher butadiene concentration (entry 5). Increasing the amount of triethylaluminium (1/1/2) resulted in the formation of pure (according to ^1H NMR spectroscopy) E-isomer (entries 6 and 7). The amount of butadiene was important only for the C_8/C_{16} ratio. Keeping the amount of triethylaluminium constant and increasing the phosphine/palladium ratio to 2/1 also yielded pure E-isomer when an equimolar amount of butadiene was used (entry 8). However, when the butadiene concentration was increased the E/Z ratio decreased, and, as expected, higher telomers were formed (entries 9–11). Increasing the amount of phosphine had a slight positive effect on the stereochemistry and suppressed the formation of C_{16} compounds (entries 12 and 13), but also resulted in inhomogeneous reaction mixtures.

The present results suggest that the high E/Z ratios observed with polymer-supported palladium catalysts are probably not due to the nature of the catalyst but to the high Al/Pd ratios in the catalysts used in these reactions. These examples also demonstrate that the amount of triethylaluminium may be further increased without any loss of configurational purity. Polymer-supported catalysts are, indeed, preferred in these reactions, since their high reactivities allow the use of a small amount of the catalyst and, consequently, a large excess of the aluminium compound.

The mechanism for telomerizations of dienes with alcohols and acids has been extensively investigated [6,7,13], but is still a matter of controversy. From reactions with secondary amines it has not yet been possible to isolate any intermediates. It may be assumed, though, that in analogy with the reaction with acetic acid [13], a *syn*-π-allyl-σ-allyl palladium intermediate is initially formed. Protonation of this complex yields a π-allyl palladium intermediate (**6**). When Nu = OAc it is claimed that this conversion proceeds with retention of the *syn* configuration [13]. The Z-product observed should, however, be formed from the *anti*-π-allyl palladium intermediate (**7**) (Scheme 1). Increasing the amount of ligand (butadiene and triphenylphosphine) should favour conversion to a σ-allyl palladium complex (**8**) and thus facilitate isomerization to the *anti* complex and, consequently, the formation of N,N-diethyl-Z-2,7-octadienylamine (**4**). Conversely, increasing amounts of



Scheme 1.

triethylaluminium favour formation of the *E*-isomer. This effect may be due to the formation of a more active catalyst, possibly a bimetallic compound, which does not allow *syn–anti* isomerization.

Experimental

All reactions were performed under purified nitrogen. Palladium(II) acetate was obtained from Engelhardt, triphenylphosphine from Merck, and butadiene from Fluka. *N,N*-diethylamine, obtained from Aldrich, was distilled from calcium hydride and stored under nitrogen. Triethylaluminium, from Fluka, was dissolved in dry toluene (2 *M* solutions) before use and the solutions were stored under nitrogen. Toluene (PA grade) was dried over calcium chloride and distilled before use.

^{1}H NMR spectra (200 MHz) were recorded on a Bruker WP 200 FT spectrometer ($CDCl_3$ as solvent and Me_4Si as internal standard).

General procedure for the reaction of butadiene with N,N-diethylamine

$Pd(OAc)_2$ (56 mg, 0.25 mmol) and PPh_3 (0.25–0.75 mmol) were placed in a Fisher–Porter autoclave equipped with a magnetic stirrer. The autoclave was flushed with nitrogen and cooled to $-78\,°C$ (dry ice-EtOH bath). Butadiene (13–42 mmol) was condensed into the autoclave and toluene (1 ml), Et_2NH (6.3 mmol) and Et_3Al (0.25–0.50 mmol) added from syringes. After the cooling bath had been removed the mixture was stirred at ambient temperature for 2 h then for 18 h at 40 °C. The mixture was diluted with diethyl ether and the amines were isolated by extraction followed by distillation in a Kugelrohr apparatus.

Acknowledgements

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