Metal Complexes in Organic Synthesis. VIII.[1,2] Allylic Alcohols as Starting Materials in Palladium-catalyzed Wittig-type Olefinizations

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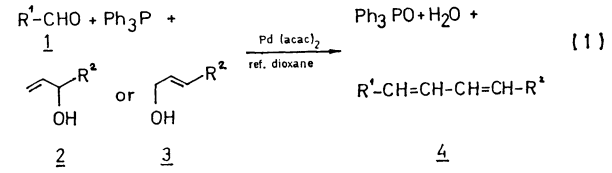
(Received July 28, 1982)

Allylic alcohols, aldehydes, and triphenylphosphine participate in a one-pot process catalyzed by palladium, which is formally equivalent to the Wittig olefinization. It can be applied to both aliphatic and aromatic aldehydes. The resulting olefins which appear as mixtures of stereoisomers were fully hydrogenated. Two different mechanisms can account for the observed results.

Palladium catalyzed and promoted reactions have attracted the interest of the chemical community since this transition metal provides us with the possibility of performing several interesting transformations.[3]

In the course of our study on the alkylation of 2,4-pentanedione with allylic and related alcohols under palladium catalysis,[4] we observed the formation of *ca.* 0.7% of (*Z*)- and (*E*)-stilbene in the reaction of sodium 2,4-pentanedionate with benzyl alcohol in the presence of catalytic amounts of bis(2,4-pentanedionato)palladium ($Pd(acac)_2$), and triphenylphosphine. Since benzaldehyde is formed together with toluene by disproportionation of benzyl alcohol, we first reasoned that the phosphine present in the reaction media could somehow react with the alcohol to yield benzyltriphenylphosphonium hydroxide, which should be the precursor of the Wittig reagent. The ylide could finally react with benzaldehyde in a conventional way.

We then started a study on the reaction of several different aldehydes with allylic alcohols and triphenylphosphine under palladium catalysis, the metal being always added in the form of $Pd(acac)_2$. The general reaction can be formulated as indicated in Eq. 1, and the results of the most significant experiments are collected in Table 1.



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Some experimentation was performed before appropriate experimental conditions could be found. Dioxane was shown to be superior as solvent to THF, DME, diglyme, and toluene. The refluxing dioxane was passed through a molecular sieve pad before returning to the reaction flask. This shortened the required reaction times although the yields were not affected. Triphenylphosphine was the most suitable phosphorus compound for this reaction since tributylphosphine, tri-*o*-tolylphosphine, tris(*o*-methoxyphenyl)-phosphine, triethyl phosphite and bis(1,2-diphenylphosphino)ethane gave clearly lower yields of condensation products.

The olefinization method has been extended to aliphatic aldehydes, both saturated and α,β-unsaturated, as well as to aromatic aldehydes with different

Table 1. The reactions of aldehydes, allylic alcohols, and triphenylphosphine in the presence of $Pd(acac)_2$[a] · structures of products **5**

Op.	Ald.	Alc.[b]	Molar ratio Ald./Alc.	Time/h	Products **4** (Yield/%)	Products **4** R_1	Products **4** R_2	Products **5**	Products **5** R_2	Products **5** R_3
1	**1a**	**2**	1.0/1.1	40	**4a**(49)	4-ClC_6H_4	*n*-C_5H_{11}	**5a**	*n*-C_5H_{11}	4-ClC_6H_4
2	**1a**	**2**	1.0/2.2	70	**4a**(68)[c]					
3[d]	**1a**	**2**	1.0/1.1	72	**4a**(49)					
4	**1a**	**3a**	1.0/5.0	75	**4b**(41)	4-ClC_6H_4	CH_3	**5b**	CH_3	4-ClC_6H_4
5	**1b**	**2**	1.0/1.1	5	**4c**(48)[e]	4-$NO_2C_6H_4$	*n*-C_5H_{11}	**5c**	*n*-C_5H_{11}	4-$NH_2C_6H_4$
6	**1b**	**3b**	1.0/1.1	5	**4d**(45)	4-$NO_2C_6H_4$	*n*-C_3H_7	**5d**	*n*-C_3H_7	4-$NH_2C_6H_4$
7	**1c**	**2**	1.0/1.1	65	**4e**(20)	4-$MeOC_6H_4$	*n*-C_5H_{11}	**5e**	*n*-C_5H_{11}	4-$MeOC_6H_4$
8	**1d**	**2**	1.0/1.1	72	**4f**(51), **4g**(4)	4-$HOCC_6H_4$[f]	*n*-C_5H_{11}	**5f**[g]	*n*-C_5H_{11}[g]	4-MeC_6H_4[g]
9	**1d**	**2**	1.0/4.0[h]	72	**4f**(65), **4g**(28)					
10	**1f**	**2**	1.0/1.1	7 d	**4h**(32)	*n*-C_5H_{11}	*n*-C_5H_{11}	**5h**	*n*-C_5H_{11}	*n*-C_5H_{11}
11[i]	**1f**	**2**-OAc	1.0/1.1	65	**4h**(30)					
12	**1g**	**2**	2.0/1.1	24	**4i** (12)[j]	MeCH=CH	*n*-C_5H_{11}	**5i**	*n*-C_5H_{11}	*n*-C_3H_7
13	**1h**	**2**	1.0/1.1	88	**4j** (27)[k]	*n*-PrCH=CH	*n*-C_5H_{11}	**5h**	*n*-C_5H_{11}	*n*-C_5H_{11}

a) One equivalent of PPh_3 and a 5% molar of Pd were used unless otherwise stated. b) 1-Octen-3-ol (**2**), (*E*)-2-buten-1-ol (**3a**), (*E*)-2-hexen-1-ol (**3b**). c) 1,3-Octadienes were also detected. d) 10% molar of Pd was used. e) 3-((*E*)-2-Octenyl)-2,4-pentanedione and 3,3-bis((*E*)-2-octenyl)-2,4-pentanedione could also be isolated.[4] f) For **4f**. See text for **4g**. g) See text for **5g**. h) Two equivalents of PPh_3 were used. i) Two drops of hydrazine were added to reduce the Pd(II). j) 2-Pentyltoluene was also detected. k) 1-Pentyl-2-propylbenzene was also detected.

substituents at the ring. 4-Chlorobenzaldehyde (**1a**), 4-nitrobenzaldehyde (**1b**), 4-methoxybenzaldehyde (**1c**), terephthalaldehyde (**1d**), phthalaldehyde (**1e**), hexanal (**1f**), (*E*)-2-butenal (**1g**), and (*E*)-2-hexenal (**1h**), were shown to react with triphenylphosphine and one or more of the following allylic alcohols: 1-octen-3-ol (**2**), its acetate (**2**-OAc), (*E*)-2-buten-1-ol (**3a**) and (*E*)-2-hexen-1-ol (**3b**). However, a simple ketone, 6-methyl-2-heptanone was recovered after refluxing in dioxane for seven days with **2**, triphenylphosphine and 5% molar $Pd(acac)_2$.

Irrespective of primary or secondary nature of the allylic alcohols, products **4** were always formed by reaction at the terminal end of the allylic system (see ops. 4 and 6 in Table 1). The regioselectivity of the reaction is always higher than 99% as shown by GLC analysis of the hydrogenated products **5** (see below).

The olefins **4** were formed as mixtures of stereoisomers. We did not study the stereochemical outcome of our reactions. However, ratios of isomers as determined by GLC are indicated in the experimental part.

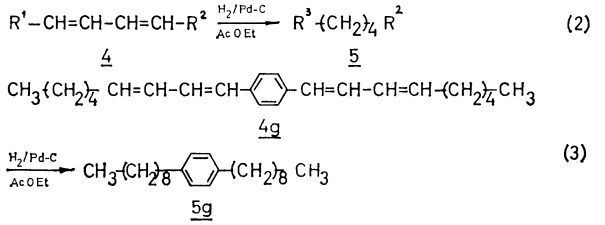
When the unsaturated aldehydes **1g** and **1h** were used as starting materials, only reaction at the carbonyl group was observed, products arising from attack at the electrophilic β position not being detected.

Terephthalaldehyde (**1d**) reacted with one equivalent of **2** to yield mainly the product of monocondensation, 1-(4-formylphenyl)-1,3-nonadiene (**4f**) (51%), and only minor amounts of the corresponding product of dicondensation, 1,4-bis(1,3-nonadienyl)benzene (**4g**) (4%) (see op. 8). Even working with a large excess of alcohol, **4f** was formed as the major product (op. 9). A similar selectivity in the reactions of the aldehyde **1d** in Wittig olefinizations has been described.[5]

In our first experiments aimed at preparing 1-(4-chlorophenyl)-1,3-nonadiene (**4a**), we realized that the reaction stopped when both the aldehyde **1a** and triphenylphosphine, but not the alcohol **2**, were still present in the reaction media. Elimination of water or acetic acid from allylic alcohols and acetates through the intermediacy of π-allylpalladium complexes is well documented[4,6] and we could demonstrate that dehydration of **2** was indeed a side reaction. In op. 2 a ratio **1a**/**2** of 1.0/2.2 was adopted, the yield of **4a** being raised to 68%. Also, the solvent, which was carefully recovered after the reaction and analyzed by GLC, showed two additional peaks. Hydrogenation under 10% Pd–C catalysis led to a dioxane containing octane as the only accompanying product, thus allowing us to assign the (*Z*)- and (*E*)-1,3-octadiene structures to the products present in the dioxane before hydrogenation.

The reactions were quite clean except when the nitroaldehyde **1b** was used. In such cases (ops. 5 and 6) no triphenylphosphine was recovered, a complicated array of products without nitro group being also formed. The reduction of nitro groups by trivalent phosphorus compounds is a well known fact[7] which can account for the observations made.

Since the olefins **4** were formed as mixtures of stereoisomers, we hydrogenated them under 10% Pd–C



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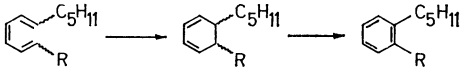
(3)

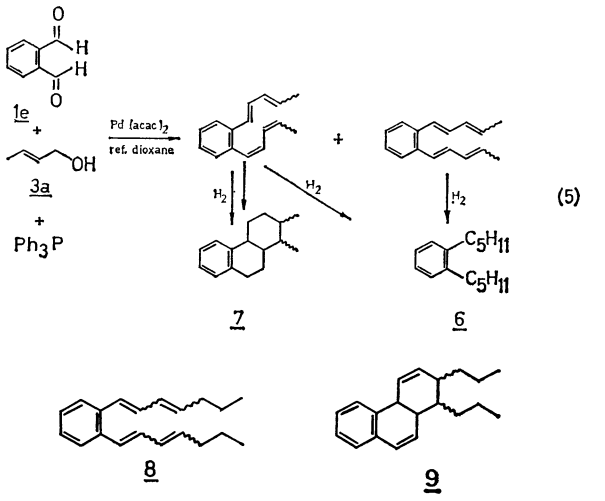
catalysis to the corresponding saturated compounds **5** as indicated in Eqs. 2 and 3. The results are collected in Table 1. Products **5** were homogeneous in GLC to an extent higher than 99%. They were fully characterized by elemental analysis and the usual spectroscopic techniques, or by comparison (GLC) with authentic specimens.

When trienes **4i** and **4j** were hydrogenated, the corresponding paraffins, dodecane (**5i**) and tetradecane (**5h**), were contaminated with *ca.* 6% of another components which presented a molecular ion in mass spectrometry at *m/e* eight units lower than the corresponding **5**, and aromatic absorptions in the ^{1}H-NMR spectrum. On these grounds the structures of 2-pentyltoluene and 1-pentyl-2-propylbenzene can be attributed to the contaminant products. They can arise from electrocyclic ring closures on the pertinent isomers of constitutions **4i** and **4j** followed by oxidative aromatization (Eq. 4).



(4)

We turned next to **1e** as starting aldehyde. Its reactions were much more complicated than those previously described. When **1e** was treated with a tenfold excess of **3a** and two equivalents of triphenylphosphine under palladium catalysis, a 17% of a complex mixture of products without carbonyl group was isolated. Also triphenylphosphine was recovered, but no **1e** could be detected in the mixture. This was hydrogenated to only two products formed in a ratio of *ca.* 2/1. Mass spectrometric analysis coupled with GLC allowed us to assign the structure of 1,2-dipentylbenzene (**6**), and the constitution of 1,2-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**7**) to the products (Eq. 5).



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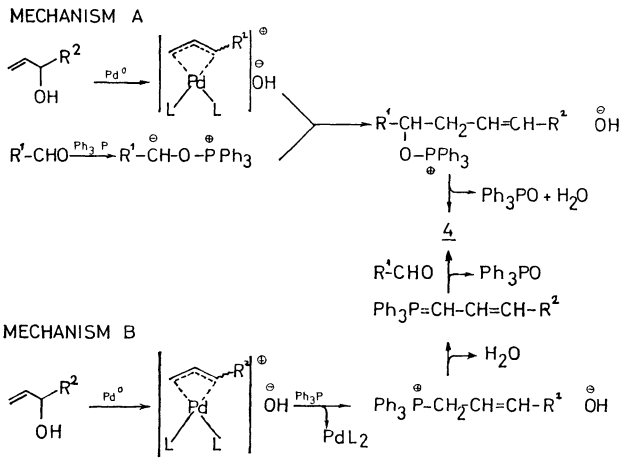

Fig. 1. Possible mechanisms accounting for the observed olefinizations.

Similar experiments were performed with **3b** as starting alcohol. In this case a 48% of diolefinization products could be isolated as a mixture of no less than eight components with the constitutions of 1,2-bis(1,3-heptadienyl)benzene (**8**), and probably 1,2-dipropyl-1,2,4a,10a-tetrahydrophenanthrene (**9**). A sample of **8** was isolated by column chromatography and inequivocally characterized by ^{1}H-NMR spectroscopy and mass spectrometry.

Two different mechanisms can account for the observed olefinizations. They are indicated in Fig. 1. Both mechanisms involve the intermediacy of π-allyl complexes formed by reaction of allylic alcohols with palladium(0) species. It should be recalled that allylic alcohols can indeed act as precursors for such complexes,[4] palladium(0) being formed by *in situ* reduction of the bivalent palladium compound really added to the reaction mixture. The inversion of reactivity at the carbonyl group needed for mechanism A to be operative has been previously postulated.[8] However, the reaction between phosphines and π-allylnickel[9] and palladium[10] complexes as exemplified by mechanism B has been described. At this point we can not decide through which mechanism the reactions proceed.

Experimental

Infrared and ^{1}H-NMR spectra were respectively recorded with a Perkin-Elmer Infracord 720 and a Perkin-Elmer R-12 models. Mass spectra were run with a Hewlett-Packard 5930 spectrometer. Only peaks with a *m/e* value above 20 are indicated unless they correspond to the molecular ion. GLC determinations were carried out in the Hewlett-Packard 5831A and Perkin-Elmer Sigma 1 models, both provided with flame ionization detection and UCW columns (0.5 m) unless otherwise stated.

Reaction between ***1a***, ***2***, *and Triphenylphosphine (op. 2); Preparation of 1-(4-Chlorophenyl)-1,3-nonadiene (****4a****).* The aldehyde **1a** (1.405 g, 10.0 mmol), alcohol **2** (2.816 g, 22.0 mmol), triphenylphosphine (2.751 g, 10.5 mmol) and Pd(acac)$_2$ (0.153 g, 0.5 mmol) were refluxed in dioxane (8 ml) for 70 h under magnetic stirring and dry nitrogen. The refluxing solvent was passed through a molecular sieve (4 Å) pad. The solvent was distilled off and the residue was chromatographed through a silica-gel column to afford **4a** (eluted with hexane), triphenylphosphine, **1a**, and triphenylphosphine oxide (eluted respectively with hexane(85)–dichloromethane(15), dichloromethane and chloroform).

4a: 1.591 g (68%). Ratio of isomer peaks in GLC: 38/15/13/34. IR (film): 1640, 1600, 980, 840, 790 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.75—1.10 (broad t, 3H), 1.10—1.75 (m, 6H), 1.9—2.4 (m, 2H), 5.50—6.95 (m, 4H), 7.25 (s, 4H). MS: *m/e* 236(7), mol wt 234(M$^+$, 30), 177(46), 163(49), 142(80), 129(100), 115(38), 96(34), 67(28), 41(44).

The distilled dioxane was analyzed by GLC showing two additional peaks in a 44/56 ratio. The mixture was treated with hydrogen at atmospheric pressure under 10% Pd–C (0.035 g) catalysis. When the uptake of hydrogen was over the catalyst was filtered off and the filtrate was analyzed by GLC. Only one additional peak was observed which was shown to correspond to octane by comparison with an authentic specimen.

The following products were prepared in a similar manner (see Table 1):

*1-(4-Chlorophenyl)-1,3-pentadiene (****4b****)*: Ratio of isomer peaks in GLC: 25/35/40. IR (film): 1640, 1590, 980, 940, 920, 840, 810, 790, 720 cm^{-1}. ^{1}H-NMR (CCl_4): δ 1.80 (d, J=6 Hz, 3H), 5.50—6.77 (m, 4H), 7.28 (broad s, 4H). MS: *m/e* 180(4), mol wt 178(M$^+$, 17), 143(67), 128(100), 115(46), 89(21), 75(25), 53(26).

*1-(4-Nitrophenyl)-1,3-nonadiene (****4c****)*: Ratio of isomer peaks in GLC: 9 (including a shoulder)/11/80. IR (film): 1630, 1590, 1510, 1330, 980 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.7—1.1 (m, 3H), 1.15—1.80 (m, 6H), 1.85—2.50 (m, 2H), 5.7—7.3 (m, 4H), 7.45, 7.60, 8.15, 8.30 (4H). MS: *m/e* mol wt 245(M$^+$, 6), 158(26), 142(50), 141(54), 137(26), 128(100), 119(48), 117(44), 115(58), 102(32), 96(40), 91(64), 83(38), 77(34), 67(36), 65(32), 63(26), 57(26), 44(76).

*1-(4-Nitrophenyl)-1,3-heptadiene (****4d****)*: Ratio of isomer peaks in GLC: 28.5/4.5/11.5/55.5. IR (film): 1640, 1580, 1510, 1340, 990, 950, 860, 740 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.92 (t, J=7 Hz, 3H), 1.15—1.80 (m, 2H), 2.15 (q, J=7 Hz, 2H), 5.5—7.2 (m, 4H), 7.30, 7.45, 8.00, 8.15 (4H). MS: *m/e* mol wt 217(M$^+$, 43), 188(36), 174(21), 143(83), 142(69), 129(50), 128(100), 115(58), 83(40), 77(23), 55(73), 41(77), 39(69).

*1-(4-Methoxyphenyl)-1,3-nonadiene (****4e****)*: Ratio of isomer peaks in GLC: 40.5/11.5/10.5/37.5. IR(film): 1610, 990, 820 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.75—1.10 (broad t, 3H), 1.1—1.8 (m, 6H), 1.85—2.65 (m, 2H), 3.78 (s, 3H), 5.45—6.83 (m, 4H), AA'BB' system centered at 7.17 (4H). MS: *m/e* mol wt 230(M$^+$, 25), 204(21), 202(32), 187(21), 173(28), 168(21), 159(32), 134(100), 121(57), 119(46), 91(34), 89(25).

*1-(4-Formylphenyl)-1,3-nonadiene (****4f****) and 1,4-Bis(1,3-nonadienyl)benzene (****4g****).* ***4f***: Ratio of isomer peaks in GLC: 42/10/13/35. IR (film): 2890, 2750, 1690, 1600, 990, 950, 860, 840, 820, 800 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.7—1.1 (broad t, 3H), 1.1—1.7 (m, 6H), 1.90—2.05 (m, 2H), 5.25—7.20 (m, 4H), 7.30, 7.45, 7.65, 7.80 (4H), 9.90 (broad s, 1H). MS: *m/e* mol wt 228(M$^+$, 12), 157(21), 143(20), 129 (100), 115(28), 91(28), 67(23), 41(20).

4g: Ratio of isomer peaks in GLC: 13/10/12/29/11/11/14. IR (film): 1640, 980, 940, 860 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.70—1.80 (m, 18H), 1.90—2.60 (m, 4H), 5.40—7.15 (m, 8H), 7.22 (s, 4H). MS: *m/e* mol wt 322(M$^+$, 7), 181(35), 167(82), 155(80), 141(100), 129(51), 128(48), 115(36), 91(20), 67(27), 55(23), 41(28).

*6,8-Tetradecadiene (****4h****)*: Ratio of isomer peaks in GLC (Carbowax 20 M column, 2 m): 71/29. IR (film): 990, 950 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.75—1.15 (m, 6H), 1.15—1.85 (m, 12H), 1.85—2.45 (m, 4H), 5.15—6.65 (m, 4H).

MS: *m/e* mol wt 194(M^+, 46), 124(25), 110(50), 109(36), 96(92), 95(78), 82(72), 81(96), 67(100), 55(21), 54(20), 41 (32).

*2,4,6-Dodecatriene (**4i**)*: Ratio of peaks in GLC: 3/6.5 (this belongs to *2-pentyltoluene*)/90.5. IR (film): 1640, 990, 940, 920 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.90 (t, J=6 Hz, 3H), 1.10—1.70 (m, 6H), 1.78 (d, J=6 Hz, 3H), 1.95—2.45 (m, 2H), 5.30—6.85 (m, 6H). MS: *m/e* mol wt 164(M^+, 19), 107(22), 105(26), 93(52), 91(61), 79(100), 77(39), 65(21), 41(26).

*4,6,8-Tetradecatriene (**4j**)*: Ratio of peaks in GLC: 23/11/7.5 (this belongs to *1-pentyl-2-propylbenzene*)/58. IR (film): 990, 960 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.7—1.2 (m, 6H), 1.20—1.75 (m, 8H), 1.8—2.6 (m, 4H), 5.2—6.6 (m, 6H). MS: *m/e* mol wt 192(M^+, 17), 121(25), 105(27), 93(42), 92(35), 91(87) 79(100), 77(50), 71(46), 67(33), 65(25), 55(21), 53 (20), 43(79).

*Hydrogenation of **4a**; Preparation of 1-Chloro-4-nonylbenzene (**5a**).* The diene **4a** (0.850 g, 3.6 mmol) in ethyl acetate (25 ml) was hydrogenated at atmospheric pressure for 20 min in the presence of 10% Pd–C (0.050 g). The catalyst was filtered off and the solvent was evaporated to yield 0.848 g (98%) of **5a**, bp 127 °C (oven temp)/0.5 mmHg (1 mmHg= 133.322 Pa), which was homogeneous in GLC. ^{1}H-NMR (CCl_4): δ 0.7—1.1 (m, 3H), 1.1—2.0 (broad s, 14H), 2.6 (t, J=7 Hz, 2H), 7.2 (m, 4H). MS: *m/e* 240(7), 239(7), mol wt 238(M^+, 20), 125(100), 91(40), 57(30), 44(47). Found: C, 75.40; H, 9.84; Cl, 15.20%. Calcd for $C_{15}H_{23}Cl$: C, 75.44; H, 9.71; Cl, 14.85%.

The following products were prepared in a similar manner (see Table 1):

*1-Chloro-4-pentylbenzene (**5b**)*: Bp 112 °C (oven temp)/0.9 mmHg, 98% yield, homogeneous to an extent of more than 99% in GLC. ^{1}H-NMR (CCl_4): δ 0.65—1.95 (m, 9H), 2.50 (t, J=8 Hz, 2H), 7.0, 7.15, 7.20, 7.35 (4H). MS: *m/e* 184(3), mol wt 182(M^+, 7), 127(29), 125(100), 91(64), 89(36), 77(22), 63(34), 51(32), 41(91). Found: C, 71.98; H, 8.29; Cl, 19.74%. Calcd for $C_{11}H_{15}Cl$: C, 72.32; H, 8.27; Cl, 19.41%.

*1-Amino-4-nonylbenzene (**5c**)*: Bp 158 °C (oven temp)/1 mmHg, homogeneous in GLC. IR (film): 3500, 3400 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.9 (t, J=5 Hz, 3H), 1.25 (broad s, 14H), 2.45 (t, J=7 Hz, 2H), 3.35 (s, 2H), 6.35, 6.50, 6.80, 6.95 (4H). MS: *m/e* mol wt 219(M^+, 13), 106(100). Found: C, 81.94; H, 11.70; N, 6.45%. Calcd for $C_{15}H_{25}N$: C, 82.13; H, 11.49; N, 6.38%.

*1-Amino-4-heptylbenzene (**5d**)*: Bp 135 °C (oven temp)/1 mmHg, homogeneous to an extent of more than 99% in GLC. IR (film): 3450, 3380 cm^{-1}. ^{1}H-NMR (CCl_4): δ 0.60—1.05 (m, 3H), 1.10—1.75 (broad s, 10H), 2.45 (t, J= 8 Hz, 2H), 3.75 (s, 2H), 6.30, 6.45, 6.70, 6.85 (4H). MS: *m/e* mol wt 191(M^+, 12), 106(100). Found: C, 81.31; H, 11.17; N, 7.41%. Calcd for $C_{13}H_{21}N$: C, 81.62; H, 11.06; N, 7.32%.

*1-Methoxy-4-nonylbenzene (**5e**)*: Bp 140 °C (oven temp)/0.5 mmHg, homogeneous to an extent of more than 99% in GLC. ^{1}H-NMR (CCl_4): δ 0.55—1.05 (m, 3H), 1.05—1.95 (broad s, 14H), 2.53 (t, J=7 Hz, 2H), 3.70 (s, 3H), AA′BB′ system centered at 6.85 (4H). MS: *m/e* mol wt 234(M^+, 5), 121(100). Found: C, 81.95; H, 11.37%. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18%.

*4-Nonyltoluene (**5f**)*: Bp 120 °C (oven temp)/0.6 mmHg, homogeneous to an extent of more than 99% in GLC. ^{1}H-NMR (CCl_4): δ 0.90 (t, J=5 Hz, 3H), 1.25 (broad s, 14H), 2.25 (s, 3H), 2.50 (t, J=7 Hz, 2H), 6.87 (s, 4H). MS: *m/e* mol wt 218(M^+, 0.5), 105(100), 41(51). Found: C, 87.92; H, 12.14%. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00%.

*1,4-Dinonylbenzene (**5g**)*: Bp 205 °C (oven temp)/0.5 mmHg, homogeneous to an extent of more than 99% in GLC. ^{1}H-NMR (CCl_4): δ 0.90 (t, J=7 Hz, 6H), 1.27 (broad s, 28H), 2.52 (t, J=7 Hz, 4H), 6.95 (s, 4H). MS: *m/e* mol wt 330(M^+, 0.3), 105(100), 92(60), 91(63), 77(21). Found: C, 87.29; H, 12.90%. Calcd for $C_{24}H_{42}$: C, 87.19; H, 12.81%.

*Tetradecane (**5h**)*: It was compared with an authentic specimen and homogeneous to an extent of more than 99% in GLC when it was produced from **4h**. However, **5h** originated from **4j** was contaminated with an 8% of *1-pentyl-2-propylbenzene* which gave peaks in MS at *m/e* 190, 91, and 77.

*Dodecane (**5i**)*: It was compared with an authentic specimen. An analysis by GLC coupled with mass spectrometry revealed that it was contaminated with a 7% of *2-pentyltoluene* which gave peaks in MS at *m/e* 162(M^+, 2), 105(77), 92(24), 91(45), 79(30), 77(35), 65(28), 55(20), 53(24), 51(30), 43(54), 41(100).

*Reaction of **1e**, **3a**, and Triphenylphosphine.* The aldehyde **1e** (1.340 g, 10.0 mmol), the alcohol **3a** (7.200 g, 0.1 mol), triphenylphosphine (5.502 g, 21.0 mmol) and $Pd(acac)_2$ (0.152 g, 0.5 mmol) were refluxed in dioxane (10 ml) for 72 h under magnetic stirring and dry nitrogen. The refluxing solvent was passed through a molecular sieve (4 Å) pad. The solvent was distilled off and the residue was extracted with hexane leaving insoluble triphenylphosphine oxide. The hexane was evaporated and the new residue was chromatographed through a silica-gel column giving 0.460 g (17%) of a hydrocarbon mixture eluted with hexane and 2.089 g of the starting phosphine eluted with hexane(4)–dichloromethane(1). All the other eluted fractions were complex mixtures of unidentified products. The hydrocarbon mixture (0.402 g, 1.9 mmol) was hydrogenated at atmospheric pressure in ethyl acetate (10 ml) in the presence of 10% Pd–C (0.040 g). The catalyst was filtered off and the solvent evaporated to afford a colourless liquid (0.409 g) which analyzed by GLC gave two peaks in a ratio 66.5/33.5. An analysis by GLC coupled to mass spectrometry was consistent with, respectively, the structure of *1,2-dipentylbenzene* (**6**) and the constitution of *1,2-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene* (**7**).

6: MS: *m/e* mol wt 218(M^+, 12), 105(100), 91(26).

7: MS: *m/e* mol wt 214(M^+, 2), 129(100), 115(21).

*Reaction of **1e**, **3b**, and Triphenylphosphine.* The aldehyde **1e** (1.340 g, 10 mmol), the alcohol **3b** (4.000 g, 40 mmol) triphenylphosphine (5.502 g, 21 mmol), and $Pd(acac)_2$ (0.152 g, 0.5 mmol) were refluxed in dioxane (10 ml) for 64 h under magnetic stirring and dry nitrogen and the refluxing solvent being passed through a molecular sieve (4 Å) pad. The solvent was evaporated and the residue was chromatographed through a silica-gel column. A mixture (1.845 g) of hydrocarbons and triphenylphosphine was eluted with hexane. Further elutions gave triphenylphosphine (0.761 g), a mixture (0.267 g) of triphenylphosphine, **3b** and unidentified products (all eluted with hexane(4)–dichloromethane(1)), **3b** (0.247 g) (eluted with hexane(7)–dichloromethane(3)), and triphenylphosphine oxide (eluted with chloroform). The mixture of hydrocarbons and triphenylphosphine was treated in benzene (25 ml) with methyl iodide (1.5 g) at room temperature for 2 h. The precipitate of methyltriphenylphosphonium iodide formed was filtered off and the remaining solution evaporated to afford 1.284 g (48%) of a mixture of *1,2-bis(1,3-heptadienyl)benzene* (**8**) and probably *1,2-dipropyl-1,2,4a,10a-tetrahydrophenanthrene* (**9**), which presented eight peaks in GLC with relative areas 10/33/13.5/5/12/9.3/6.8/10.4. A further chromatography through

a silica-gel column gave 0.052 g of pure **8**.

8: ^{1}H-NMR (CCl_4): δ 0.95 (t, J=7 Hz, 6H), 1.10—1.80 (m, 4H), 2.15 (dt, J *ca.* 6 and 6 Hz, 4H), 5.40—6.90 (m, 8H), 6.95—7.60 (m, 4H). MS: *m/e* mol wt 266(M^+, 12), 183(34), 181(37), 167(100), 166(27), 165(47), 155(28), 153 (34), 152(32), 141(97), 128(53), 115(37), 91(26), 79(25), 77(20), 67(25), 55(31).

The authors express their gratitude to the "Comisión Asesora de Investigación Científica y Tecnica" and to "INAPE" (Ministerio de Educación y Ciencia of Spain) for financial support and for a grant (to A. T.). The authors are also indebted to Dr. P. de March and A. Virgili for kindly registering the mass spectra.

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