ORGANIC CHEMISTRY

REACTION BETWEEN ISOPRENE AND ANILINE ON COMPLEX PALLADIUM CATALYSTS

E. A. Petrushkina and L. I. Zakharkin

UDC 542.97:66.095.2:547.315.2:547.551

Isoprene and aniline have been reacted on the catalytic system $Pd(acac)_2-Ph_3P$ to form a mixture of isomeric telomers: N-(dimethyloctadien-2,7-yl-1)anilines and N-(dimethyloctadien-1,7-yl-3)anilines but on the catalytic system $Pd(acac)_2-Ph_3P-CF_3COOH$ the main product is a mixture of N-(methylbuten-2-yl)aniline adducts. The reaction between N-methylaniline and isoprene on the latter catalyst also gives a mixture of N-methyl and N-(methylbuten-2-yl)aniline adducts.

Keywords: *catalytic telomerization, terpenoid anilines.*

The reaction between isoprene and aniline catalyzed by palladium complexes provides a convenient way of synthesizing terpenoid compounds. The composition of the reaction products is extremely sensitive not only to the type of catalyst used and its modification but also to the nature of the amine [1-7]. In the case of dialkylamines [1-5] a mixture of N,N-(dimethyloctadien-2,7-yl)dialkylamines is formed containing all four possible ways of joining the two isoprene molecules: head to tail, tail to head, head to head, and tail to tail. Isoprene–amine adducts are also formed in this process but in very small amounts [4]. The reaction between aromatic secondary amines and isoprene on the catalytic system (CS) $Pd(acac)_2-R_3P$ is quite different from the reaction with dialkylamines. Diphenylamine does not usually react with isoprene [4] and N-methylaniline is less reactive than dialkylamine. On the CS $PdCl_2-Ph_3P$, in contrast to the dialkylamines, N-methylaniline reacts with isoprene to give adducts only [6]. Ammonia [2] and monoalkylamines [7] react with isoprene to give a mixture of N-(dimethyloctadien-2,7-yl-1)amine telomers as well as a mixture of N-(dimethyloctadien-1,7-yl-3)amine telomers, which are not formed with secondary amines. Telomers of the latter type as well as N-(dimethyloctadien-1,7-yl-3)arylamines make possible the transformation to 2-(dimethyloctadien-2,7-yl)anilines using the Claissen rearrangement of amino groups. These are an interesting class of terpenoid compounds in which an acyclic 1-terpene group is linked to the aromatic ring.

TABLE 1. Composition of Products of Reaction between Isoprene and Aniline in MeOH* and MeCN† Solution on CS A and B

CS (ratio $C_6H_8:H_2NPh$)	Isoprene conversion 1-10(%)	Yield (%)		Component content of catalysate (%)										
		Σ_{1-6}	Σ_{7-10}	telomers						adducts				Other (unidentified)
				1	2	3	4	5	6	7	8	9	10	
A* (1 : 1)	67	100	-	61	10.7	12.4	5.6	10.2	—	—	—	—	—	-
A* (2 : 1)	64	100	-	59.7	10.9	12.9	6.3	10.2	—	—	—	—	—	-
A† (2 : 1)	48	77.5	11.8	13.7	61.1	-	-	-	25.2	50.0	40.0	10.0	-	10.7
B* (2 : 1)	20	-	100	-	—	—	—	-	—	13.3	67.0	4.0	6.1	10.1
B† (2 : 1)	21.5	5.4	78.8	25	25	50	-	-	—	10.9	79.8	1.7	7.6	15.8

A. N. Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, 117813 Moscow. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 8, pp. 1794-1798, August, 1992. Original article submitted October 24, 1991.

TABLE 2. PMR Spectra of Individual Products (in $CDCl_3$, δ, ppm, internal standard HMDS)

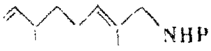
1*	0.93 d (3 H, CH_3); 1.29 m (2H, CH_2); 1.56 s (3H, CH_3); 1.97 – 2.04 m (4 H, $-CH_2-CH_2-$); 3.48 s (2 H, $-CH_2-N\langle$); 4.88 – 4.93 m (2H, $CH_2=$); 5.32 t (1H, $-CH=$); 5.50–5.52 m (1H, $=CH-$); 6.52 m (3H, C_6H_5); 7.05 m (2 H, C_6H_5)
2*	1.55 m (2H, $-CH_2-$); 1.65 and 1.69 s.s (6H, CH_3, CH_3); 2.01 m (4H, $-CH_2-CH_2-$); 3.63 s (2H, $-CH_2-N\langle$); 4.64 and 4.68 s.s (2H, $=CH_2$); 5.42 t (1H, $CH=$); 6.60 m (3H, C_6H_5); 7.14 m (2H, C_6H_5)
7*	1.55 d (3H, CH_3); 1.61 s (3H, CH_3); 3.55 s (2H, $-CH_2-N\langle$); 5.43 q (1H, $CH=$); 6.60 m (3H, C_6H_5); 7,10 m (2H, C_6H_5)
8*	1,64 and 1.71 s.s (6 H, CH_3, CH_3); 3.64 d (2 H, $-CH_2-N\langle$); 5.29 t (1H, $CH=$); 6,61 m (3H, C_6H_5); 7.14 m (2 H, C_6H_5)
9*	1.23 d (3 H, CH_3); 1.70 s (3 H, CH_3); 3.82 q (1 H, CH); 4.77 and 4.95 s.s (2 H, $CH_2=$); 6.61 m (3 H, C_6H_5); 7.10 m (2 H, C_6H_5)
10†	1.65 and 1.66 s.s (12 H, $CH_3\times4$); 3.81 d (4 H, $-CH_2-N-CH_2$); 5,16 t (2 H, $CH=$, $CH=$); 6.60–6.66 m (3 H, C_6H_5); 7.10–7.16 m (2 H, C_6H_5)
11†	1.52 s (3H, CH_3); 1.55 d (3H, CH_3); 2.83 s (3 H, $^NCH_3$); 3.70 s (2H, $-CH_2-N\langle$); 5.26 q (1 H, $CH=$); 6.66 and 7.16 m.m (5H, C_6H_5)

---

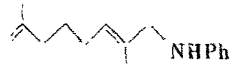
*Bruker WP-200 SY instrument.

†Varian VXR-400 instrument.

In connection with this we investigated the reaction between aniline and isoprene on the Cs $Pd(acac)_2-R_3P$ (A) and $Pd(acac)_2-R_3PCF_3-COOH$ (B) in MeOH and MeCN solution. We found that a mixture containing a large number of products was formed having compositions of both 2:1 and 1:1 while both N-(dimethyloctadiene-2,7-yl-1)anilines **1-4** and N-(dimethyoctadien-1,7-yl-3)anilines **5**, **6** were present in the mixture of telomers **1-7**.



(1)

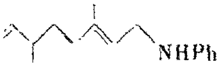


(2)

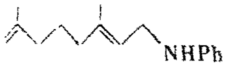
(7)

(8)

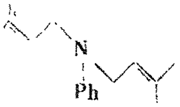
(9)



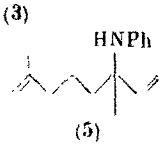
(3)



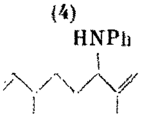
(4)



(10)



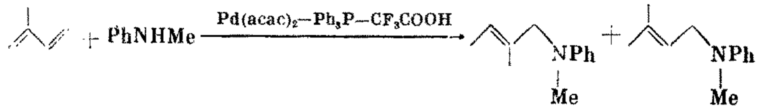
(5)



(6)

Table 1 illustrates the conversion of isoprene and the percentage composition of the products in MeOH and MeCN solutions on CS A and B. The structures of telomers **1** and **2** and of the adducts **7-10** were found from their PMR spectra (Table 2), but those of telomers **3-6** were found indirectly from a comparison of their GLC retention times with those of the corresponding isoprene telomers obtained previously with dialkyl- [3] and alkylamines [7]. It can be seen from Table 1 that in MeOH solution telomerization proceeds smoothly to give telomers **1-6** with isomer **1** being the predominant one. In MeCN solution together with the terpenoid isomers **1-6**, with **2** the predominant one, a small amount of an isoprene aniline adduct forms. Unfortunately, the anilines **5** and **6** are only formed in small amounts. The use of CS B gives mainly isoprene aniline adducts **7-10**, the predominant isomer being **8**. In contrast to this alkyl- and dialkyl-amines give mainly telomers of type **1-6** on CS B [5, 7]. Dialkylamines only give isoprene amine adducts on CS B where CF_3COOH has been replaced by a stronger acid, for example CF_3SO_3H [5]. This investigation into the telomerization of isoprene and aniline shows that aniline is more reactive in this reaction than alkylamines [7] and N-methylaniline [6] under similar conditions.

We compared the behavior of N-methylaniline and aniline in their reactions with isoprene on CS B and found that in the case of N-methylaniline the predominant reaction is formation of adducts according to the scheme



(11) (12)

In this case the greatest yield of adducts is obtained with MeCN solution. The structure of adduct **11** follows from its PMR spectrum (Table 2).

EXPERIMENTAL

Monomers of 99% purity were used in the investigation. GLC analysis was conducted on a Model 3700 instrument with a capillary column ($l = 25$ m), stationary phase SE-54, and with programmed heating from 60 to 280°C at 8°C/min, using n-$C_{21}H_{44}$ as a standard. PMR spectra (see Table 2) were recorded on Bruker WP-200SY and Varian VXR-400 instruments.

Telomerization of Isoprene and Aniline in MeOH Solution. In a stream of argon 1 mmole $Pd(acac)_2$, 2 mmoles Ph_3P, 30 ml MeOH, 300 mmoles isoprene, and 300 (or 150) mmoles aniline (and in the case of CS B 10 mmoles CF_3COOH) were placed in a flask fitted with a magnetic stirrer and boiled for 30 h. The solvent was evaporated off and the residue distilled *in vacuo* and analyzed by GLC. The isomers were separated by highly efficient fractional distillation *in vacuo*. For the mixture of isomers **1-6**: Found, %: C 83.55; H 10.35; N 5.96. $C_{16}H_{23}N$. Calculated, %: C 83.78; H 10.11; N 6.10. For the mixture of adducts **7-10**: Found, %: C 81.72; H 9.25; N 8.61. $C_{11}H_{15}N$. Calculated, %: C 81.93; H 9.37; N 8.68.

Telomerization of Isoprene and Aniline in MeCN Solution. In a stream of argon 1 mmole $Pd(acac)_2$, 4 mmoles $(BuO)_3P$, 25 ml MeCN, 400 mmoles isoprene, and 200 mmoles aniline (and in the case of CS B, 10 mmoles CF_3COOH) were placed in a glass ampul. The sealed ampul was heated for 32 h at 80°C. The solvent was evaporated off and the residue distilled *in vacuo* and analyzed by GLC.

Reaction between Isoprene and N-Methylaniline in MeOH Solution. In a stream of argon 1 mmole $Pd(acac)_2$, 2 mmoles Ph_3P, 30 ml MeOH, 300 mmoles isoprene, 300 mmoles N-methylaniline, and 10 mmoles CF_3COOH were placed in a flask fitted with a magnetic stirrer and boiled for 30 h. The solvent was evaporated off and the residue distilled *in vacuo* and analyzed by GLC. Yield: 30%, comprising 48% isomer **11** and 52% isomer **12**.

Reaction between Isoprene and N-Methylaniline in MeCN Solution. In a stream of argon 1 mmole $Pd(acac)_2$, 4 mmoles $(BuO)_3P$, 25 ml MeCN, 400 mmoles isoprene, 200 mmoles N-methylaniline, and 10 mmoles CF_3COOH were placed in a glass ampul. The sealed ampul was heated for 32 h at 80°C. The solvent was evaporated off and the residue distilled *in vacuo* and analyzed by GLC. Yield: 77%, comprising 33% isomer **11** and 67% isomer **12**.

REFERENCES

1. N. Hidai, H. Mizuta, K. Hirai, and J. Uchida, *Bull. Chem. Soc. Jpn.*, **53**, 2091 (1980).
2. W. Keim and M. Röper, *J. Org. Chem.*, **46**, 3702 (1981).
3. L. I. Zakharkin, E. A. Petrushkina, and L. S. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 4, 886 (1983).
4. W. Keim, K. Kurtz, and M. Röper, *J. Mol. Catal.*, **20**, 129 (1983).
5. W. Keim, M. Röper, and M. Schieren, *J. Mol. Catal.*, **20**, 139 (1983).
6. L. I. Zakharkin and E. A. Petrushkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1344 (1986).
7. E. A. Petrushkina, V. I. Bregadze, Yu. F. Oprukenko, and A. V. Orlinkov, *Metallorg. Khim.*, **5**, No. 3, 683 (1992).