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Telomerization of Isoprene with Dialkylamine Catalyzed by Palladium Complexes

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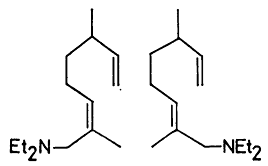
Synopsis. Telomerization of isoprene with diethylamine in the presence of catalytic amounts of palladium chloride and triphenylphosphine under carbon dioxide and/or using methanol as solvent gave three kinds of 2:1 adducts in good yields, one of which was found to be an adduct of new type.

Many transition metal complexes have been shown to catalyze the reaction of 1,3-butadiene with alcohols,(1) carboxylic acids,(2) amines,(3) water,(4) and active methylene and methylidyne compounds(5) yielding mainly 2,7-octadienyl derivatives (2:1 adducts). However, the analogous reactions of isoprene have not been well studied. The reaction of morpholine with isoprene by nickel complexes was reported to give mainly 1:1 adducts along with a small amount of 2:1 adducts.(3) This is in sharp contrast to the ready formation of 2:1 adducts from butadiene and amines with a variety of transition metal complexes. Recently Tanaka *et al.*(6) reported that butyllithium catalyzed telomerization of isoprene which led to formation of (2*Z*)-*N*,*N*-dialkyl-3,7-dimethyl-2,6-octadienylamine in a good yield.

We reported in a previous paper the synthesis of citronellol starting from isoprene through a 2:1 adduct with methanol.(7) We wish here to describe the reaction of isoprene with diethylamine catalyzed by palladium complexes, where carbon dioxide and methanol showed a remarkable effect on the product distribution.

Results and Discussion

Treatment of isoprene with diethylamine in the presence of $PdCl_2$ and triphenylphosphine under carbon dioxide and/or using methanol as solvent gave 2:1 adducts of isoprene and the amine, together with a small amount of 1:1 adducts and isoprene dimers. The 2:1 adducts were found to be a mixture of three octadienyl derivatives **1**, **2**, and **3**. Their structures have been determined on the basis of the infrared and NMR spectra after their separation by preparative GLC (Table 1). The product **1** gives rise to two quartets at 2.38 and 2.40 ppm in the NMR spectrum assignable to the methylene protons of the diethylamino group, indicating that the product **1** is a mixture of *E*- and *Z*-isomers around the trisubstituted C=C bond. On the other hand, measurement of the nuclear Overhauser effect in the 270 MHz ^1H NMR spectra of the products **2** and **3** clearly showed that they have an *E*-configuration around the trisubstituted C=C bond. Thus, the integrated intensity of the olefinic proton ($-CH_2-C\underline{\underline{H}}=$) of **2** at 5.35 ppm increased *ca.* 16% by irradiating the methylene protons between the C=C bond and the nitrogen atom, whereas the intensity increased only *ca.* 1.8% by irradiating the methyl protons attached to the C=C bond at 1.71 ppm.



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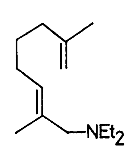

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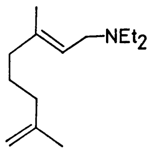

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A standard procedure was adopted to study the effect of a number of parameters on the conversion of isoprene and the product ratio (Table 2). The reaction at 100 °C for 24 h under nitrogen without solvent gave only a 14% conversion into a mixture of 1:1 adducts, the adduct **2**, and isoprene dimers. However, the same reaction under carbon dioxide gave a 85% conversion to yield products comprising *ca.* 60% of the 2:1 adducts. The striking feature of this reaction is a large amount of the 2:1 adducts formed under nitrogen when alcohols such as methanol and ethanol were used as solvent. Methanol is especially effective among them and the reaction proceeds smoothly even at room temperature.

Carbon dioxide is effective not only in accelerating the reaction rate, but also in changing the product ratio. When the reaction was run in methanol at 100 °C under nitrogen, the ratio of the adducts **1**, **2**, and **3** was 20:44:28. However, the reaction under carbon dioxide changed the ratio into 40:32:13. The product ratio is also dependent upon the reaction temperature. The high temperature seems to favor the formation of the adducts **2** and **3**, and disfavor the formation of **1** when the reaction was run in methanol.

Among the 2:1 adducts obtained here, the compound **3** is an adduct of new type. The adducts with methanol corresponding to the compounds **1** and **2** are readily produced by using zero-valent palladium complexes as catalyst.(8) Use of a zero-valent palladium complex, $Pd(DBA)_2$ (DBA=dibenzylideneacetone), instead of $PdCl_2$ in the above amination reaction in methanol gave the 2:1 adducts of both diethylamine and methanol in low yields. On the other hand, in the early stage of the reaction in the presence of $PdCl_2$ and triphenylphosphine in methanol at room temperature, the adducts with the amine were only produced, while the adducts with methanol were not obtained at all. These results strongly suggest that a zero-valent complex may not be involved as an active species and that the adducts with the amine are not formed *via* the adducts with methanol, although Hata *et al.*(9) previously reported the exchange reaction of the allylic groups of ethers with a variety of active hydrogen compounds including secondary amines by using palladium complexes. It is of great interest to note that $Pd(DBA)_2$ coupled with diethyl ammonium chloride repressed the formation of the adducts with

Table 1. IR and NMR data of the products **1**, **2**, and **3**

Products	IR (cm^{-1})	NMR (δ values from TMS)
1	1640 ($\nu_{C=C}$), 905, 1000 (δ_{C-H} of the vinyl group)	0.94 (3H, d, J=7.0 Hz, $\underline{CH_3}$-CH⟨), 0.96 (6H, t, J=7.5 Hz, $\underline{CH_3}$-CH_2-N), 1.30 (2H, q, J=7.5 Hz, ⟩CH-$\underline{CH_2}$-), 1.70 and 1.84 (3H, 2×s, =C($\underline{CH_3}$)-), 1.85—2.20 (3H, m, =CH-$\underline{CH}$⟨ and -$\underline{CH_2}$-CH=), 2.38 and 2.40 (4H, 2×q, J=7.5 Hz, CH_3-$\underline{CH_2}$-N), 2.86 and 2.91 (2H, 2×s, ⟩N-$\underline{CH_2}$-$\overset{\vert}{C}$=), 4.7—5.1 (2H, m, $\underline{CH_2}$=CH-), 5.1—5.9 (2H, m, =$\underline{CH}$-).
2	1640 ($\nu_{C=C}$), 895 (δ_{C-H} of the terminal methylene)	0.96 (6H, t, J=7.5 Hz, $\underline{CH_3}$-CH_2-N), 1.25—2.70 (2H, m, -CH_2-$\underline{CH_2}$-CH_2-), 1.63 (3H, s, CH_2=C($\underline{CH_3}$)-), 1.71 (3H, s, -CH=C($\underline{CH_3}$)-), 1.7—2.2 (4H, m, -$\underline{CH_2}$-CH_2-$\underline{CH_2}$-), 2.41 (4H, q, J=7.5 Hz, CH_3-$\underline{CH_2}$-N), 2.87 (2H, s, =$\overset{\vert}{C}$-$\underline{CH_2}$-N⟨), 4.74, (2H, s, $\underline{CH_2}$=C⟨), 5.35 (1H, t, J=7.5 Hz, -$\underline{CH}$=).
3	1645 ($\nu_{C=C}$), 895 (δ_{C-H} of the terminal methylene)	0.99 (6H, t, J=7.5 Hz, $\underline{CH_3}$-CH_2-N), 1.1—1.5 (2H, m, -CH_2-$\underline{CH_2}$-CH_2-), 1.56 (3H, s, -CH=C(-$\underline{CH_3}$)-), 1.62 (3H, s, CH_2=C($\underline{CH_3}$)-), 1.7—2.2 (4H, m, -$\underline{CH_2}$-CH_2-$\underline{CH_2}$-), 2.44 (4H, q, J=7.5 Hz, CH_3-$\underline{CH_2}$-N), 3.00 (2H, d, J=7.0 Hz, ⟩N-$\underline{CH_2}$-CH=), 4.72 (2H, m, $\underline{CH_2}$=), 5.34 (1H, t, J=7.0 Hz, -$\underline{CH}$=).

Table 2. Telomerization of isoprene with diethylamine

Catalyst[a)]	Atmosphere	Solvent (Temp)	Conv. (%) of Isoprene	Product (%)					
				1	**2**	**3**	1 : 1[b)] adducts	Isoprene[c)] dimers	Methanol adducts
$PdCl_2$	N_2	none (100)	14	tr	25	—	40	34	0
$PdCl_2$	CO_2	none (100)	85	10	48	7	8	26	0
$PdCl_2$	N_2	MeOH (100)	100	20	44	28	4	4	0
$PdCl_2$	CO_2	MeOH (100)	100	40	32	13	15	tr	0
$PdCl_2$	N_2	EtOH (100)	100	11	65	16	1	6	0
$PdCl_2$	N_2	MeOH (28)	100	53	33	11	3	tr	0
$Pd(DBA)_2$	N_2	MeOH (28)	43	17	28	tr	tr	28	27[d)]
$Pd(DBA)_2$ -$Et_2N^+H_2Cl^-$	N_2	MeOH (28)	46	69	31	—	tr	tr	0
$Pd(DBA)_2$ -$Me_4N^+I^-$	N_2	MeOH (28)	26	29	36	—	—	23	11[e)]

a) In all cases, an equimolar amount of triphenylphosphine was added to the palladium complexes. b) The 1 : 1 adducts were mainly composed of *N*,*N*-diethyl-2-methyl-2-butenylamine and *N*,*N*-diethyl-3-methyl-2-butenylamine. c) The isoprene dimers predominantly contained 2,7-dimethyl-1,3,7-octatriene. d) The adducts were 1-methoxy-2,6-dimethyl-2,7-octadiene (9%) and 1-methoxy-2,7-dimethyl-2,7-octadiene (18%). e) The adducts were the same as above d), 4 and 9% respectively.

methanol. This may suggest intervention of proton in the above amination reaction, which may originally come from methanol or diethylcarbamic acid formed from the amine and carbon dioxide, and formation of a positively charged π-allyl intermediate similar to that proposed by Åkermark *et al.*[10)]

Experimental

All reactions were performed under oxygen-free conditions. Alcohols and isoprene were dried and distilled over anhydrous $CaSO_4$. Diethylamine was purified by distillation over potassium or sodium hydroxide pellets. Bis(benzylideneacetone)palladium $Pd(DBA)_2$ was prepared according to the procedure reported by Ishii *et al.*[11)]

Analysis was carried out with a Hitachi K23 gas chromatograph (He carrier gas through 2 m×3 mm in stainless-steal column, 10% Silicone DC 550) and a Shimadzu GC-5A chromatograph for all preparative GLC (He carrier gas through 2.1 m×10 mm in stainless-steal column, 10% Silicone DC 550). NMR spectra were obtained with a Hitachi Perkin-Elmer 90 MHz instrument using tetramethylsilane (TMS) as internal standard and C_6D_6 as solvent. IR spectra were recorded on a Hitachi 215 instrument.

General Procedure at 28 °C. In a 100 ml two neck flask or a 75 ml Pyrex glass ampule, in which palladium chloride (88.7 mg, 0.5 mmol) and triphenylphosphine (131.1 mg, 0.5 mmol) were placed, isoprene (15 ml, 150 mmol), diethylamine (15 ml, 144 mmol), and methanol (15 ml, 370 mmol) were added in this order. After stirring for 24 h at 28 °C, the reaction gave a 100% conversion into **1** 53%, **2** 33%, **3** 11%, and 1:1 adducts (3%). A mixture of **1**, **2**, and **3** was obtained by distillation (103—105 °C/933 Pa) and separated by preparative GLC at 150 °C. Found: C, 80.52; H, 13.40; N, 6.71% for **1**; C, 80.32; H, 13.16; N, 6.80% for **2**; C, 80.56; H, 13.24; N, 6.51% for **3**. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69%. IR and NMR spectra are summarized in Table 1.

This general procedure was used for the series of experiments with changes in conditions as summarized in Table 2. The reactions at 100 °C and/or under carbon dioxide were achieved in a 100 ml stainless-steal autoclave for 24 h.

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